METALS AND METALLIC COMPOUNDS

BY

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IN FOUR VOLUMES

VOLUME I

INTRODUCTION, METALLOGRAPHY, ELECTRO-CHEMISTRY

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PREFACE

During the past few years so much fruitful research work has been carried out in metallography, crystallography, electrochemistry, colloid chemistry, and geo-chemistry that we are enabled to approach the subject of metals in an altogether new spirit. It is now possible to suggest reasons for phenomena which at one time appeared inexplicable, and to detect regularities where once the facts seemed chaotic. Advantage should surely be taken of the new aspect of the subject in the textbooks. The traditional practice of giving long "catalogues of salts" and empirical accounts of metallurgical processes, is no doubt of use for books of reference. But in books intended for continuous reading, such a method is far too uninspiring, and should be abandoned now that knowledge has advanced sufficiently to offer something better.

In this book, an attempt is made to correlate cause and effect, and to introduce such theoretical views as will serve to connect the known facts in an ordered and elegant sequence. The book is intended for the advanced student of inorganic and metallurgical chemistry, and for those engaged in research in these subjects. The industrial chemist will, I hope, also find it of assistance, whilst certain portions (e.g. those dealing with work-hardening, recrystallization, the effect of impurities on metals, and corrosion) should prove useful to the engineer.

The difficulties which I have experienced in writing the book have served to convince me that the work is really needed. Much information which I regard as being of the greatest importance I have found scattered through the recent volumes of the scientific and technical journals—in many cases in journals which are not commonly considered as being devoted to chemistry at all, and which appear sometimes to have escaped the notice of the writers of standard chemical textbooks.

Of the four volumes, the first is of a generalized character. It begins with an introduction in which I have endeavoured to condense the elementary principles of general chemistry, physics and geology, a knowledge of which the reader is assumed in the body of the work to possess. The body of Volume I is divided into two parts, "The Study of the Metallic State" (Metallography) and "The Study of the Ionic State" (Electrochemistry). The metallographic portion includes the effects of deformation, annealing and alloying on the properties of metals; the electrochemical portion includes such subjects as the structure of precipitates, the colloidal state, electro-deposition and corrosion; it closes with a chapter on radioactivity. By the treatment of the metallography and electrochemistry of metals in a general fashion, with examples chosen from individual metals, these two subjects are presented in a more satisfactory manner than if they were introduced piecemeal in the sections devoted to the different metals. In addition, a great deal of wearisome repetition is avoided in the subsequent volumes.

The chapters dealing with electrochemistry have presented special difficulties. I do not believe it possible to obtain a proper understanding of the chemistry of metals without some knowledge of electrochemistry and colloid chemistry. In order to throw open these subjects to all, I have made the treatment, as far as possible, non-mathematical. A great obstacle to the attractive presentation of electrochemical principles is the barbarous character of the nomenclature in use; I have not felt justified in introducing a new nomenclature, but have tried to make the best of the existing terms, selecting a terminology which will be definite, even if it is not dignified.

In Volumes II, III and IV, I deal one by one with the individual metals. The order observed is based upon the Periodic Table in a form similar to that made popular by Sir James Walker. The old form of the Periodic Table which classes sodium along with copper has now—it is to be hoped—few active supporters, although it still ornaments the walls of our lecture theatres, and appears to find favour with the authors of chemical treatises based upon the classical model. In the new table, which accords well with the chemical and electrochemical properties of the elements and is in harmony with modern ideas of the structure of the atom, the elements can be divided into three main classes, and I have allocated a different volume to each class. Volume II deals with the metals of the "A Groups," Volume III with the "Transition Elements" ("Group VIII" of the old table), whilst Volume IV deals with the metals of the "B Groups."

The space devoted to each metal is divided into three main sections. The first deals with the metal and its compounds from the point of view of the academical laboratory. The pure chemistry of the metal and its compounds is here discussed; no reference to ores, technical processes and industrial application is made in this section, which is therefore fairly concise. The section ends with a summary of the methods of analysis of the metal in question, although the book is not intended as a practical analytical handbook.

The second section deals shortly with the terrestrial occurrence of the metal in question, starting with its origin in the rock-magma, and discussing the probable mode of formation of the important ores and minerals, both primary and secondary.

The third section—which is often the longest—is of a technical character. We start with the ore or mineral, and follow the metal through the processes of concentration and smelting, and finally consider the practical uses of the element, and of compounds containing it; I have tried to show why the properties of the individual metal—as stated in the theoretical section—render it suitable for the various uses to which it is put, and to make the technical section a correct survey of industry carried on at the present time; I have only referred to obsolete methods of procedure in a few places where such a reference is thought to be instructive.

Stress has been laid on the important points, which have been illustrated by a few chosen examples in order to avoid burdening the reader with a mass of names and numbers, which he will not retain, and which can be looked up when required in a table of physical constants or in a detailed book of reference. Proper names have largely been concentrated in the footnotes, and thus kept out of the text; I have written a book about chemistry—not about chemists. Likewise the figures are frankly diagrammatic, drawn to emphasize the salient points; in the diagrams of technical plants much that is of merely structural importance is omitted. I have only employed the historical order of description where it happens also to be the logical order.

Throughout the book numerous references are given, in footnotes, to scientific and technical literature; these should be consulted by the reader who wishes to study any given part of the subject in greater detail. In selecting these references, I have not given preference to the work of the actual originators of the various theories or processes, but have sought rather to provide the reader with the most recent information regarding the matter under discussion. The recent papers themselves will include references to the earlier ones, whilst the converse is clearly not true.

In subjects regarding which disagreement prevails at present, I have in most cases departed from the usual custom of giving in turn a summary of the views advanced by the various disputants, as this practice is apt to leave the reader hopelessly bewildered. Rather, I have endeavoured to suggest a standpoint which the average reader may safely adopt as a working hypothesis, until further research finally decides the question under dispute. If, however, the subject happens to be one of special interest to the reader, he should consult the references in the foot-notes, and form his own opinions. In these foot-notes, he will find references to many authorities whose views are not held by the present writer.

As already stated, great efforts have been made to render the book as "up-to-date" as possible, but I have not concealed the fact that uncertainty still prevails on many parts of the subject, and that research is continually being conducted to settle these doubtful points. I have endeavoured to prepare the reader to revise his own opinions without undue reluctance every time he may open a scientific journal.

I wish to return thanks to the numerous friends who have very kindly given information or advice. Especially would I mention Mr. C. T. Heycock, Dr. E. K. Rideal, Prof. H. C. H. Carpenter, and Mr. Maurice Cook. Mr. Cook has prepared the micro-photographs accompanying Volumes I, III and IV of the book, and has shown much skill and patience in obtaining results which illustrate clearly the points described in the text.

U. R. E.

CAMBRIDGE, 1923.

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LIST OF JOURNALS REFERRED TO IN VOLUME I AND ABBREVIATIONS EMPLOYED

Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Amer. Machinist	American Machinist.
Analyst	Analyst.
Ann. Phys.	Annalen der Physik.
Annales Physique	Annales de Physique.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deutsch. Phys. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Biochem. J.	Biochemical Journal.
Brit. Assoc. Rep.	British Association for the Advancement of Science, Report.
Bull. Soc. Chim.	Bulletin de la Société chimique de France.
Bull. Wisconsin Univ.	Bulletin of Wisconsin University.
Carn. Schol. Mem.	Carnegie Scholarship Memoirs (Iron and Steel Institute).
Chem. News	Chemical News.
Chem. Soc. Ann. Rep.	Chemical Society, Annual Report.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker-Zeitung.
Chem. Zentralblatt	Chemisches Zentralblatt.
Comptes Rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Discovery	Discovery.
Electrician	Electrician.
Electrochem. Ind.	Electrochemical Industry.
Electrotech. Zeitsch.	Elektrotechnische Zeitschrift.
Engineer	Engineer.
Engineering	Engineering.
Eng. Min. J.	Engineering and Mining Journal.
Gazetta	Gazetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Int. Ass. Test. Mat.	International Association for Testing Materials.
Int. Zeitsch. Met.	Internationale Zeitschrift für Metallographie.
Int. Cong. App. Chem.	International Congress of Applied Chemistry.

Jahrbuch Radioakt. Elekt.	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Inst. Met.	Journal of the American Institute of Metals.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. Phys.	Journal de Chimie physique.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Met.	Journal of the Institute of Metals.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Prakt. Chem.	Journal für praktische Chemie.
J. Roy. Soc. Arts	Journal of the Royal Society of Arts.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Koll. Zeitsch.	Kolloid-Zeitschrift.
Koll. Chem. Beihefte	Kolloid-chemische Beihefte.
Le Radium	Le Radium.
Metallurgie	Metallurgie.
Met. Chem. Eng.	Metallurgical and Chemical Engineering (also called "Chemical and Metallurgical Engineering").
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University.
Mitt. Kgl. Mat. Prüfungsamt	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Phil. Mag.	Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Rev.	Physical Review.
Phys. Zeitsch.	Physikalische Zeitschift.
Proc. Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials.
Proc. Amst. Acad.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Opt. Conv.	Proceedings of the Optical Convention.
Proc. Phys. Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.

Proc. Univ. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Rec. Trav. Chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. Met.	Revue de Métallurgie.
Roy. Astr. Soc., Notices	Royal Astronomical Society, Monthly Notices.
Schweiz. Chem. Zeit.	Schweizerische Chemiker Zeitung.
Science	Science.
Sci. Progr.	Science Progress.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
Sitzungsber. Bayer. Akad.	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu München.
Sitzungsber. Preuss. Akad.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Smithson. Misc. Coll.	Smithsonian Miscellaneous Collections.
Stahl u. Eisen	Stahl und Eisen.
Svensk. Kem. Tidskr.	Svenska Kemisk Tidskrift.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Elect. Eng.	Transactions of the American Institute of Electrical Engineers.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Soc. Eng.	Transactions of the Society of Engineers.
U.S. Bur. Stand. Bull.	United States Bureau of Standards Bulletin.
Zeitsch. Angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. Anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Metallkunde	Zeitschrift für Metallkunde.
Zeitsch. Phys.	Zeitschrift für Physik.
Zeitsch. Phys. Chem.	Zeitschrift für Physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. Wiss. Photo.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.

NOTE ON MICRO-PHOTOGRAPHS IN FRONTISPIECE.

Prepared specially by Mr. MAURICE COOK, M.Sc.

Fig.

A. **Cadmium.** Section. Etched with chromic acid + nitric acid. Magnification × 60.

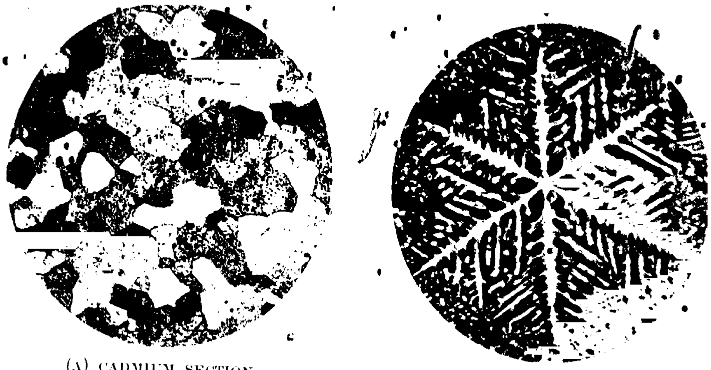
B. **Cadmium.** Free upper surface of ingot. Not etched. Magnification × 93.

C. **Lead,** slightly bent to develop slip bands. Free upper surface of ingot. Not etched. Magnification × 60.

D. **Copper-silver alloy** (60 % Ag, 40 % Cu). Section. Etched with ferric chloride + hydrochloric acid. Magnification × 440.

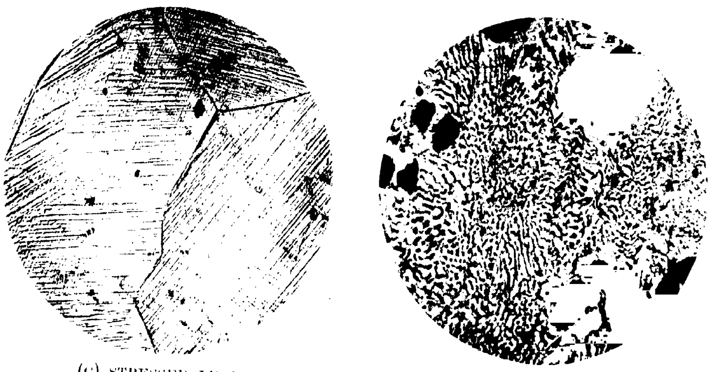
E. **Copper-nickel alloy** (70 % Cu, 30 % Ni) *as cast.* Section. Etched with chromic acid + nitric acid. Magnification × 100.

F. **Copper-nickel alloy** (70 % Cu, 30 % Ni). *Annealed* for 18 hours at 1000° C. Section. Etched with chromic acid + nitric acid. Magnification × 60.



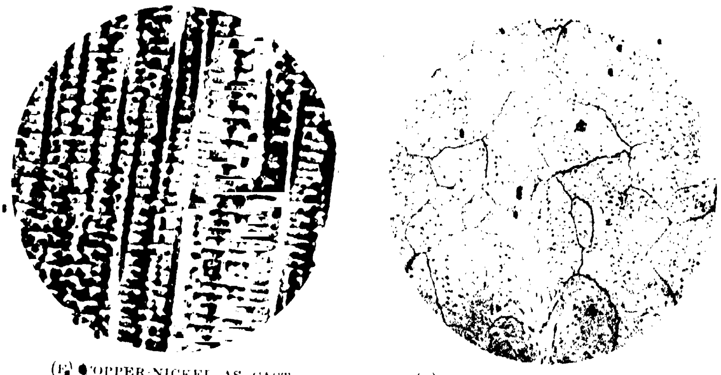
(A) CADMIUM SECTION

(B) CADMIUM SURFACE



(C) STRESSED LEAD

(D) COPPER-SILVER



(E) COPPER-NICKEL AS CAST

(F) COPPER-NICKEL ANNEALED

(For preparation see page xii)

Evans', Metals Vol. II.

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METALS AND METALLIC COMPOUNDS

INTRODUCTION

The object of this introduction is to set forth very briefly—and in a non-mathematical form—the general knowledge of chemistry, physics and geology which, in the body of the book, the reader is assumed to possess. It is intended primarily to refresh the memory of those whose study of these subjects has not been continuous, and to make them acquainted with some useful conceptions which have appeared during recent years.

Only those portions of the subject are included which are indispensable to the reader who wishes to make an intelligent study of metals and metallic compounds, and in the interests of economy of space, they are treated as shortly as possible. Much of the prevailing confusion of thought existing in connection with metallic substances is due to the fact that the necessary knowledge of general chemistry, physics and geology is not acquired before the student passes to the particular study of metals. However, those who feel themselves sufficiently familiar with any parts of the subjects discussed in the introduction will be fully justified in omitting these portions. Indeed, some readers may prefer, in the first instance, to omit the introduction altogether, and to commence their reading at page 135, referring back to the introduction where they find it necessary. From page 135 onwards, it is recommended that reading should be continuous.

Owing to the fact that, in the introduction, a vast range of subjects must be considered within a limited space, it is impossible adequately to describe the experimental basis or the process of reasoning which has led to the theoretical views on physics, chemistry and geology now generally held; the writer has been content merely to give an outline of those views in so far as they are needed for the understanding of the properties of metals and their compounds.

I. ELECTRICITY

The Electric Current. Electrical ideas are so frequently used in chemistry—and especially in the chemistry of metals—that it is necessary for every chemist to have a clear idea of the elementary principles of electricity. Contrary to the common custom, we shall commence with the consideration of an electric current as furnished by a primary cell. If a carbon plate and a zinc plate are partly immersed in dilute sulphuric acid containing potassium dichromate, and are then joined outside the liquid by a long piece of copper wire, a current of electricity is caused to flow through the wire, as is well known. The causes that underlie the generation of the current are dealt with in the latter portion of this volume. All that is desired at this point is to give the reader a useful picture of the movement of electricity that is involved.

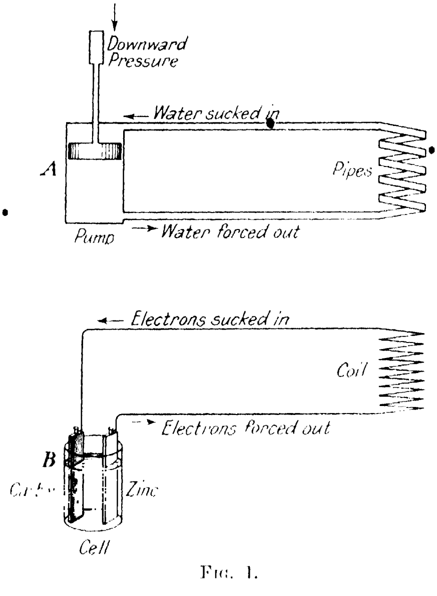

FIG. 1.

The passage of the electric current along the wire may be compared to the circulation of water through a pipe system, the analogy between the two cases being shown in Figs. 1A and 1B. If a steady downward pressure is applied to the handle of the pump shown in Fig. 1A, water will be forced out on one side into the pipe-circuit, and an equal amount sucked in on the other side. The rate of circulation through the pipe depends on the force applied to the handle, the immediate cause of the circulation being the difference of pressure produced on the two sides of the piston.

Now compare the action of the "dichromate cell," shown in Fig. 1B. It is believed that the cell forces out along the wire a stream of electrons (or particles of negative electricity) at the zinc pole (the so-called "Negative Pole"), and that it sucks in an equal number at the carbon pole (the so-called "Positive Pole"). This flow round the circuit must be considered as due to something analogous to the difference of pressure existing on the two sides of the piston in the pump. We say, therefore, that a **Difference of Potential** (or P.D.) exists between the zinc and carbon plates, and we look upon this Potential Difference as the cause of the movement of electrons round the circuit. The Potential Difference is commonly measured in *volts*; the "dichromate cell," described above, produces a P.D. of 2·12 volts; but the Daniell cell (consisting of plates of zinc and copper, immersed in solutions of their respective sulphates) is responsible for a P.D. of only about half this value, namely, 1·096 volts. The P.D. of a cell is also spoken of as the **Electro-motive Force** (E.M.F.), the force that drives the current round the circuit, or simply as the "Voltage."

Now, in the case of the water-circuit, the quantity of water that flows does not depend merely on the pressure applied to the pump-handle, but also to the length and diameter of the pipe. If the pipe is a short and stout one, a small pressure will serve to push round a great deal of water each second, whilst, if the pipe be very long or very thin, the flow is obstructed, and the same pressure applied to the pump produces a much smaller circulation of water. Exactly the same thing happens in the case of the electric circuit; if the copper wire is short and stout, the cell will give a high current; but if the length of the wire is increased, or the cross-section reduced, the current is to a corresponding extent diminished. The **strength of electric current**—which is proportional to the number of electrons flowing past a given point in the circuit each second—is in practice measured in "*amperes*." It is found that the current (C) sent out by a cell over a given circuit is proportional to the Potential Difference (E) provided by the cell in question; this is known as *Ohm's Law*, and may be expressed,

$$C \propto E.$$

Thus, since the dichromate cell has about twice the E.M.F. of the

Daniell cell, the former will force about twice as much current over the same long thin piece of wire as will the latter.[1] The magnitude of the E.M.F. required to force a current of one ampere over a given circuit is a measure of the **resistance** of that circuit; resistance is measured in *ohms*. If we express the E.M.F. of a cell in volts, the current produced by the cell in amperes, and the resistance (R) of the entire circuit in ohms (including the internal resistance of the cell), Ohm's Law may be written

$$C = \frac{E}{R}.$$

The reciprocal of the resistance is the "**conductivity,**" which is measured in "mhos" or "reciprocal ohms." The conductivity of a circuit expressed in mhos is numerically equal to the number of amperes which are forced over it by an E.M.F. of one volt; if the resistance of a circuit is R ohms, its conductivity is $\frac{1}{R}$ mhos.

The resistance of a circuit does not depend merely on the dimensions of the bodies composing it, but also on their nature. If, for instance, the copper wire of the circuit described above is replaced by an iron wire having identical dimensions, a much smaller current is forced through it by the same cell. In other words, iron has a lower conductivity—or a higher resistance—than copper; the **specific resistance** of a material is the resistance of a piece 1 cm. long, and of 1 sq. cm. cross-section. The table below gives the specific resistances of a few common materials:—

		Specific Resistance.
Copper (Annealed)		$1{\cdot}59 \times 10^{-6}$
Iron (Wrought)		$9{\cdot}0 \times 10^{-6}$
Carbon (Graphite)	varies from	4×10^{-4} upwards
5% Hydrochloric Acid		$2{\cdot}53$
Pure Water (freed from dissolved substances—Weiland)		$1{\cdot}40 \times 10^{7}$
Paraffin Wax		3×10^{18}

The current C which is forced by an E.M.F. of E volts through a conductor of length *l* cms. and cross-section *a* sq. cms. made of a material of specific resistance, *k*, will be, by Ohm's Law,

$$C = \frac{E}{R} = \frac{E}{k\frac{l}{a}} = \frac{Ea}{kl} \text{ amperes.}$$

Those substances which have a very low specific resistance are called **conductors**. The metals are by far the best conductors of electricity, and among them silver and copper have the lowest resistance. Apart from the metals, few solid substances conduct electricity well, the most important exception being carbon, which is a very useful conductor for many purposes.

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[1] It is assumed for simplicity that the resistance of the external circuit is high compared to that of the cells.

Many substances such as glass, porcelain, oil, wax, rubber, resin and ebonite do not conduct electricity to any appreciable extent. They are used to support, or to cover, the metallic conductors along which electricity flows, with a view to preventing leakage, and are therefore called **insulators.** Air and other gases can generally be regarded as good insulators, although if the potential difference between two conductors separated by air is fairly high a certain appreciable leakage of electricity does take place across the air-space; and, if the E.M.F. is raised higher still, the electricity may jump across a considerable length of air as a spark.

Solutions of salts, acids and bases in water constitute a third class of substances. They conduct electricity, but suffer chemical decomposition in the process, and are therefore called **electrolytes.**

The Effects of an Electric Current. The passage of a current through a conductor is made manifest in various different ways, which will be mentioned in turn :—

(1) **The Heating Effect.** The whole circuit is heated by the passage of a current, but the heating is most intense where the resistance is highest; if part of the circuit consists, for instance, of a very thin filament of tungsten, this may become so hot as to give out light—a fact which is utilized in the electric **glow lamp.** The heating effect of a current is also employed in the **electric furnace.**

(2) **The Chemical Effect.** Many solutions are decomposed when electricity passes through them; thus, when a current is forced through a solution of nickel chloride, it becomes split up into nickel and chlorine, which appear at the points where the electron stream enters and leaves the solution. The chemical effect of a current—of which advantage is taken in electro-plating and many other branches of industry—is fully discussed in the latter part of the present volume.

(3) **The Magnetic Effect.** If a coil of insulated wire is wound round a bar of iron, and a current is passed round the coil, the bar becomes a "magnet" and acquires the power of attracting other pieces of iron. Much of the magnetism is lost when the current is turned off, but a portion always remains. If the bar is of soft iron, it is liable to lose this "residual magnetism" on keeping, especially if subjected to rough usage. But if the bar is of hard

steel, it will retain its attractive power well, and can be taken out from the coil and used as a **permanent magnet.**

The attractive power of a magnet for iron is more or less confined to the ends of the bar (the "poles"). If a bar-magnet be suspended at its centre by a string, it sets itself with the poles in a certain direction (nearly north and south) determined by the magnetism possessed by the earth. The poles can thus be classified as "north" and "south" poles. If a second magnet be brought near to the suspended magnet, it is found that two like poles (e.g. two north poles) will repel one another, whilst two unlike poles (one north and one south) will attract one another.

The magnetising effect of a current is used in electric bells, in numerous telegraph and telephone instruments, and in electro-magnets. The electric motor is another application of the same principle.

If two circles of wire be suspended, and an electric current be passed through them, it will be found that they attract one another if the current is passing in the same direction in both circles, but that they repel one another if it is passing in opposite directions. This phenomenon is closely connected with the magnetising power of the electric current; the circles may, in fact, be regarded as two very short and stout magnets.

Furthermore, if a suspended or pivoted coil is placed between the poles of a U-shaped permanent magnet and a current is passed through it, the coil will tend to set itself with its axis parallel to the line joining the poles. This effect is employed, in the "**Moving-coil Galvanometer**" (Fig. 2A), for the measurement of a current. The current to be measured is made to pass through the pivoted coil, the movement of which is controlled by a spiral spring; a pointer is attached to the coil, which, moving over a suitable engraved scale, indicates the strength of the current passing through the instrument.

The scale may be engraved to indicate the strength of the current in amperes directly; such an instrument is then called an "**ammeter.**" The resistance of an ammeter should be *low*, so as to add as little as possible to the total resistance of the circuit.

Since the current passing through any galvanometer is determined by the P.D. which drives the current through it, the scale of a galvanometer can, as an alternative, be engraved so as to show the voltage applied to it. Such an instrument then constitutes a **voltmeter.** Only a galvanometer of *high* resistance should properly be used as a voltmeter for reasons which will be explained later; unfortunately, many so-called "voltmeters" have not nearly such a high resistance as would be desirable.

A single galvanometer of intermediate resistance and extreme sensitiveness can be made to function at will either as a **low resistance ammeter**, or as a **high resistance voltmeter**, by means of accessory wire coils of suitable resistance. If a coil of high resistance compared to that of the galvanometer be placed "in series" with it, as shown in Fig. 2B, only a fraction of the total potential drop between T and T′ falls over the galvanometer proper, and the combination becomes a high resistance voltmeter of medium sensitiveness. If, on the other hand, a coil having a resistance low compared to that of the galvanometer be connected as a "shunt" (see Fig. 2C), only a fraction of the total current passes through the galvanometer, and the combination becomes a low-resistance ammeter of medium sensitiveness. The scale of the galvanometer is made to read volts or amperes directly, allowance being made, of course, for the effect of the series or shunt resistances.

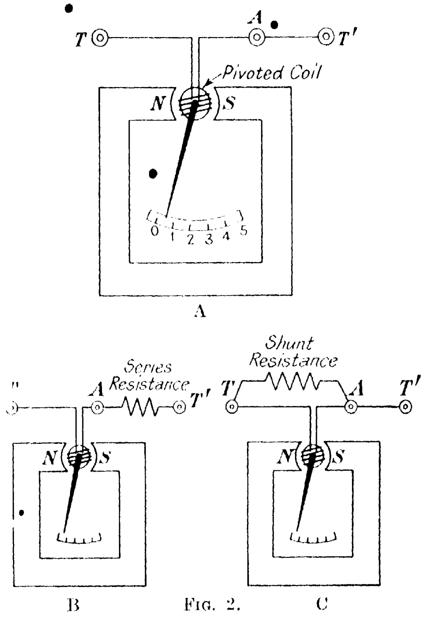
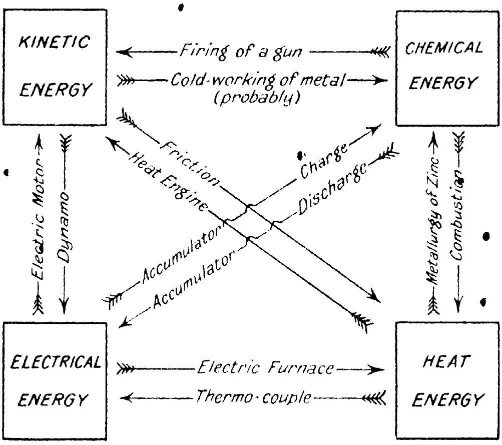


Fig. 2.

Energy. Any body or system of bodies which is in motion, or is capable of producing motion, is said to possess energy. A moving train possesses **kinetic energy**, by virtue of its motion. A mass of water in a reservoir at a high level possesses **potential energy**, for, whilst flowing down to a low level, it can be made to drive a water turbine. A heap of coal possesses **chemical energy**, since it can be burnt to produce **heat energy**, which in its turn can be used to cause motion in a steam-engine. The electric cell furnishing a current—as described above—possesses **electrical energy**, for the current can be used to drive a motor.

Different forms of energy can be transformed to one another. The following table shows the name of some machine, or some operation, in which the various transformations are carried out:—



All these forms of energy are convertible to one another, according to a definite "rate of exchange." Electrical energy, as will shortly be explained, is conveniently measured in joules; heat energy is measured in calories, a calorie being the amount of heat needed to raise the temperature of a gram of water by 1° C. If we convert electrical energy to heat energy, we always find that one joule produced 0·24 calories of heat, however the transformation is effected. The same sort of relationship applies to other transformations of energy. Apparent exceptions are easily explained. For instance, if we are converting electric energy to mechanical energy, one electric motor may prove of more value than another; but this is not because the "rate of exchange" is different in the two motors, but because the less efficient motor allows more of the electrical energy to be converted to heat, thus diminishing the amount converted into mechanical energy. The energy is not lost; it is merely converted into a form which is not desired.

"Heat" is, in fact, a form of energy which is continually appearing when not desired. It is commonly said to be a "degraded" form of energy, because it is only possible to convert it to other forms to a limited extent. When, for instance, we attempt to convert heat energy into motion in a "Heat Engine," we find that the conversion is only partial. However perfect and frictionless the engine may be, it is found that only a fraction of the heat taken up in the "hot reservoir" (e.g. the boiler) can ever be converted into mechanical energy. The remainder passes, unconverted, into the "cold reservoir" (e.g. the condenser).

The designer of machinery is mainly concerned with the avoidance of accidental conversion of energy into heat. The conversion of kinetic energy to heat through friction is minimized by the lubrication of the bearings. The conversion of electrical energy to heat is reduced by keeping low the resistance of the conductors, and in other ways. But in no machine is the appearance of heat entirely prevented.

Sources of Electrical Energy. In some countries the electrical energy which is required for industrial and domestic purposes is derived from the potential energy of water at places where a stream descends rapidly from a high to a low level (e.g. at a waterfall); the water can be made to drive a water turbine, which in turn will drive the dynamo that generates the electric current. But in countries where there are no streams with beds of steep gradient, electricity is usually derived from the chemical energy of coal. The coal may be burnt beneath boilers, and the steam utilized in driving steam-engines which work the dynamos. Alternatively, the coal can be used for the manufacture of a combustible gas, suitable for consumption in internal combustion engines, which will serve to drive the dynamos. In either case only a small portion (perhaps 10 to 25 per cent.) of the energy stored in the coal actually appears as electrical energy; the rest is lost in the form of heat energy at some stage in the transformation. Attempts to carry out the direct conversion of coal energy to electrical energy have hitherto failed.[1]

Practically the whole of our electrical energy is thus generated by means of the dynamo; that machine, which cannot be described in detail at this point, will be referred to again in the section on magnetism in Volume III. It may be mentioned, however, that at most large modern generating stations the electric current generated by the dynamos is not a continuous current, but alternating current, the direction of the movement of the electrons in the circuit being reversed at frequent intervals, perhaps fifty times each second. The different methods of transmitting electrical energy (as one-phase or three-phase alternating current) will be referred to again in Volume III.

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[1] For history of these attempts, see E. K. Rideal and U. R. Evans, *Trans. Faraday Soc.* **17** (1921), 466.

For certain purposes, especially where it is desired to utilize the "chemical effect" of electricity, the alternating current—being a mere surging of electrons to and fro about their mean positions—is useless; a continuous current, in which the electrons travel forward steadily in a single direction, is demanded, and for such cases continuous-current generators can be provided. *Small* quantities of electrical energy, if generated as continuous current, can be stored conveniently by means of the lead or nickel accumulators, described respectively in the sections on lead (Vol. IV) and nickel (Vol. III); there is no effective method of storing *large* quantities of electrical energy. Often it is convenient to use a series of lead accumulators (previously charged by means of a dynamo) to provide current in cases where only a small E.M.F. (less than, say, 12 volts) is called for; the accumulators provide a very steady E.M.F., which is usually a great advantage. Where a larger E.M.F. is required, the current is commonly provided directly by a continuous-current dynamo. Although an accumulator is certainly the most economical—and usually the most convenient—method of obtaining a steady E.M.F. of a few volts only, "primary cells" are often used for this purpose, especially for the lighting of small pocket torches. One form of primary cell (the "dichromate cell") was mentioned at the beginning of this section, and other more portable forms will be described subsequently. In all forms of primary cells, however, the production of current depends upon the oxidation of metallic zinc; since the zinc has previously been brought to the metallic condition by reduction with coal, the electrical energy generated by primary cells is ultimately derived from the chemical energy of coal. But this method of transforming coal energy to electrical energy is far more wasteful even than that in which a heat engine is employed; probably not more than 3 per cent. of the energy of coal is recovered in the form of electricity.

Units of Quantity, Energy and Power. It is possible to show that the energy required to force a volume of water, V, round the water-circuit shown in Fig. 1A is equal to

$$P \cdot V$$

where P is the difference of pressure on the two sides of the piston. Similarly the energy needed to force a quantity of electricity round the electric circuit of Fig. 1B is the product of the "potential lifference " (E) which causes the circulation, and the quantity of ectricity (Q) forced round the circuit. Thus the electrical energy s equal to

$$E \times Q$$

ut Q, the quantity of electricity, is equal to the strength of current, , multiplied by the time t, during which it flows. The energy is herefore equal to

$$ECt$$

he " Power," or rate of production of energy, is equal to

$$\frac{\text{Energy}}{\text{Time}} = \frac{ECt}{t} = EC.$$

It is now necessary to become familiar with the units of " Quantity f Electricity," " Power " and " Electrical Energy " commonly mployed ; all are simply related with the units of Current, Potential nd Resistance which have been introduced above :—

The Unit of the Quantity of Electricity is the **Coulomb** or **mpere-Second.** One coulomb of electricity passes a point on he circuit each second, when a current of one ampere is flowing. he charge of a single electron is only about $1{\cdot}59 \times 10^{-19}$ coulombs.

The Units of Power. The **Watt** is the Power developed when ne volt forces a current of one ampere round a circuit ; the power s always obtained in watts by multiplying the current (measured n amperes) by the E.M.F. (measured in volts).

The **Kilowatt,** often a more convenient unit, is equal to 1,000 vatts. One Kilowatt is equivalent to about 1⅓ horse-power.

The Units of Electrical Energy. The **Joule,** or **Watt-Second,** he energy expended when one watt is exerted for one second, is n inconveniently small unit. The **Kilowatt-Hour** (K.W.H.), he energy expended when a kilowatt is exerted for an hour, is qual to $3{\cdot}6 \times 10^6$ joules, and is the unit by which electric energy s bought and sold.

Distribution of Potential over a Circuit. If the external ircuit of a cell consists of one long uniform wire, the potential lrop along it is uniform, as expressed graphically in Fig. 3A. If, owever, part of the circuit be composed of thinner wire, or of less onducting material than the rest, the potential gradient will be steeper over the poor conductor, as shown in Fig. 3B. In the xtreme case, when one portion of the circuit consists of a very thin onductor (e.g. a lamp filament), the remainder being stout wire, practically the whole of the 2·12 volts furnished by the cell may fall over the filament; such a state of affairs is shown in Fig. 3c. The current C is constant throughout the circuit; and since, by Ohm's Law, $C = \frac{E}{R}$, it follows that E, the Potential Difference falling over any given portion, is proportional to R, the resistance of that portion.

If the internal resistance of the cell be appreciable compared to that of the external circuit, an appreciable fraction of the Potential Difference will fall within the cell: thus, in measuring the E.M.F. of a cell with a voltmeter, it is essential to employ a voltmeter the resistance of which is *high* compared to that of the cell in question.

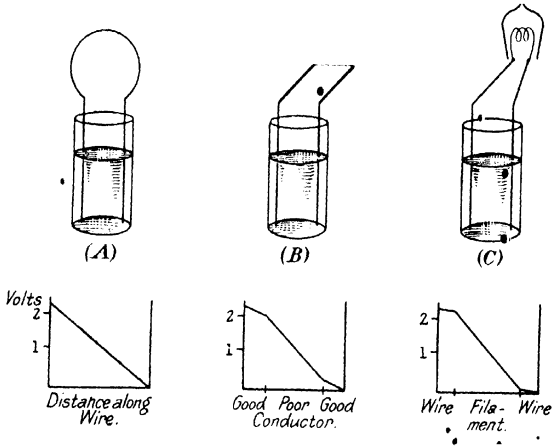

FIG. 3.

Generalized Form of Circuit. Electricity is used for all sorts of purposes; but, almost always, the apparatus is joined up in the same sort of way. It will be convenient at this point to show the general arrangement of a circuit (Fig. 4).

First of all, we require a **source of current.** This may consist of a row of cells such as have been described above; if so they will probably be joined "in series," the zinc of one cell being joined to the copper of the next, and the outside terminals of the two cells at each end of the series being joined to the external circuit. In the diagram a "battery" of three cells joined in series is shown; they will give three times the E.M.F. of one cell, but will not furnish quite three times the current, because the resistance of the extra cells will be added to that of the circuit. Often in practice, however, the source of current does not consist of primary cells, but " accumulators " ; if the E.M.F. required is more than about 12 volts, a " dynamo " will probably be used.

From Z, the so-called " negative " terminal of the source of current, the electron-stream passes to a **variable resistance** consisting of a coil of wire wound on a long frame made of an insulating material ; a sliding contact moves along the coil, and by regulating the position it is possible, at will, to make the current pass through any desired fractional part of the coil ; the electron-stream next passes through an **ammeter,** A, and thence to the " work," and finally is sucked into the " source of current " at the so-called " positive " terminal, C. A small switch, S, is usually inserted in the circuit, which allows the current to be interrupted at will.

The " work " is, of course, the apparatus or machine which it is desired to operate by means of the current ; it may be an **electric furnace,** a **plating-bath,** or a **motor.** A **voltmeter** is shown joined up " in parallel " with the " work," and is used to indicate the potential difference applied to it ; the reading of the voltmeter will not in general be as great as the full E.M.F. of the cells or dynamo, because part of the potential difference provided by the cells or dynamo will fall over the variable resistance, and probably another part over the interior of the source of current.

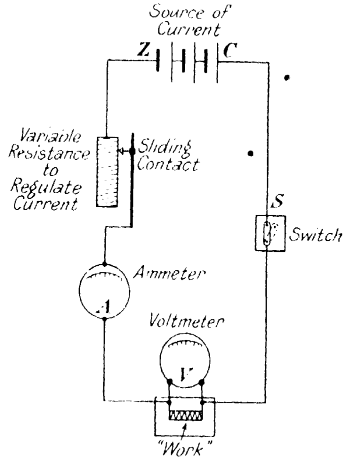

FIG. 4.

The object of the variable resistance is to enable the operator to adjust the current, until the ammeter shows that the desired amount is flowing through the " work." It should be noticed that, of the current passing through the ammeter, a certain fraction leaks through the voltmeter, and does not pass through the " work " ; if, however, the resistance of the voltmeter be high compared to that of the " work," this will be a negligible quantity.

Free Electrons. There is still a little uncertainty regarding the way in which the electron-stream passes through a *metallic* *conductor.*[1] It is, however, significant that we have independent (chemical) reasons for thinking that, in a metal, some of the electrons are by no means firmly fixed to the atom; the description given at the commencement of this section, which suggests that a stream of more or less free electrons passes through the interior of a metallic conductor when an E.M.F. is applied, is probably very near to the truth. We also know that the atoms of non-metallic substances do not readily part with their electrons, and it is significant that such substances are practically non-conductors of electricity.

Concerning the passage of electricity through a *gas* we have much more definite knowledge. It has already been stated that gases are not conductors of electricity in the same sense as metals, but that if a high E.M.F. is applied to two metal plates separated by air or other gas, a considerable discharge takes place across the space. If the pressure of the gas between the plates is very greatly reduced, charged particles known as "cathode ray particles" are expelled at high velocity from the surface of the negative pole, or "cathode," into the exhausted space between the plates. These cathode ray particles are nothing but free electrons. By means of careful experiments upon cathode rays and similar phenomena, the properties of free electrons—or "atoms of negative electricity" as they have been called—have been studied in detail; their mass and charge are both well known.

Electrostatic Charges. Electrons are believed to enter into the composition of all substances, being important constituents of every kind of atom. The ubiquitous character of electrons is suggested by the well-known and very general phenomenon of "electrification by friction"; if glass be rubbed with silk, or sealing-wax with flannel, both the rubbed object and the rubber are found to be "charged" with electricity, and have the property of attracting light objects. One substance has become "positively charged," the other "negatively charged." The so-called negatively charged substance has, it is thought, an excess of electrons over its normal quantity, whilst the so-called positively charged body has a corresponding deficit. The frictional method of producing electrification is of far less practical utility than the methods which generate a steady current, but the former method has led to our knowledge of the laws of static charges, as opposed to those of currents. It is found that two bodies charged with opposite electrifications (one being positively, one negatively charged attract each other; but that like charged bodies repel each other. The law is, of course, closely analogous to that relating to the forces between magnetic poles.

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[1] The subject is discussed by Sir J. J. Thomson, *J. Inst. Met.* **14** (1915), 3 and by C. A. F. Benedicks, *J. Inst. Met.* **24** (1920), 7. The interesting view of F. A. Lindemann, *Phil. Mag.* **29** (1915), 127, may be studied with advantage.

Free electrons are also evolved spontaneously from **incandescent bodies**. They are generated when **ultraviolet light** strikes on a metal placed in a highly exhausted vessel. Finally, they are produced continuously as streams of "β-ray particles" from many of the **radio-active substances** considered in the last chapter of this volume.[1]

Thermo-electricity. At the present stage it is convenient to refer to the thermo-couple, which was mentioned above in the table of energy-transformation processes, as an instrument in which heat energy is converted to electrical energy. Whilst, however, only an academic interest is attached to the thermo-couple as a producer of electrical energy, it possesses considerable practical importance (in the form of the thermo-electric pyrometer) as an instrument for measuring temperatures at a range too high for the use of ordinary thermometers.

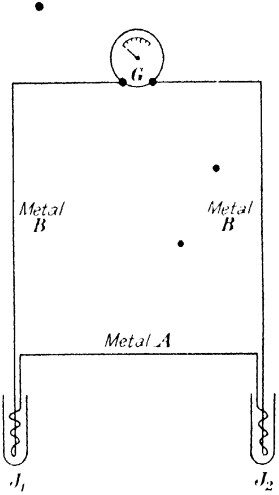

FIG. 5.

When two metals are in contact, there generally exists at the common surface a potential difference, the magnitude of which depends on the temperature. In the arrangement shown in Fig. 5, an electric circuit is made up of wires composed of two metals A and B, which are united together in two places, J_1 and J_2. If these two junctions are kept at the same temperature, the P.D. between A and B at J_1 is exactly balanced by the P.D. between B and A at J_2, and there is no resultant E.M.F. If, however, J_2 is hotter than J_1 the P.D. at J_1 will not be equal to that at J_2, and a current will be produced which will cause a deflection in the galvanometer G. Assuming that the metals A and B have been suitably chosen, the E.M.F. of the combination will increase steadily as the temperature difference is increased; and if the cold junction, J_1, is kept at a constant temperature, the magnitude of the deflection can be utilized to indicate the temperature of the other junction, J_2.

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[1] The connection between these different ways of electrification is discussed by I. Langmuir, *Trans. Amer. Electrochem. Soc.* **29** (1916), 125. Reference may also be made with advantage to J. A. Crowther's Book on "Ions, Electrons and Ionising Radiations" (Arnold).

The arrangement used in practice for measuring temperatures is a little more complicated, but depends on the same principle. The matter will be discussed further in Chapter III, which deals with pyrometry.

II. The Elements and their Modes of Combination

Chemical Combination. Elements and Compounds. The infinite number of materials with which man is acquainted may be regarded as built up by the combination of a limited number of substances which, having for many decades defied the efforts of chemists to break them up further, have been styled "elements." Recent investigations in radioactivity make it impossible to continue to define an element as "a substance which *cannot* be broken up by any means"; but those investigations have not altered the fact that it is convenient, for nearly all purposes, to regard the eighty-six elements as being the ultimate materials from which all other materials ("compounds") are built up.

When two elements combine to form a **compound,** the majority of the properties of the elements disappear; the compound usually resembles neither element. This loss of identity is the main characteristic of **chemical combination** as opposed to mere admixture.

For instance, when sodium—a metallic-looking substance, which is violently attacked by water—combines with chlorine—a greenish, odorous, highly reactive gas—the product is sodium chloride, a white, crystalline, soluble salt possessing neither the physical appearance nor the high reactivity of either component. Probably the only property which the constituents retain entirely unchanged in the combined state is their mass; the mass of sodium chloride produced is found to be equal, within the limits of experimental error, to the sum of the masses of sodium and chlorine used up.

Such a case may be compared with the admixture of ethyl alcohol and methyl alcohol; when equal weights of these substances are stirred together, the product has properties exactly intermediate between those of the components; the specific volume, for instance, of the mixture lies exactly half-way between the specific volumes of ethyl alcohol and methyl alcohol.[1] No appreciable shrinkage or expansion occurs on mixing.

Two extreme instances have been given; in certain cases, admixture is accompanied by indications of chemical reaction, but the formation of a definite compound is not easily established. If equal masses of chloroform and ether are mixed, the product has a volume which is not the sum of the volumes of the components, but no very violent transformation of properties occurs.[1] In such doubtful cases, the evolution (or absorption) of heat is a useful sign that some sort of chemical change is occurring. When chlorine acts on sodium, the substances get so hot as to emit light. When chloroform and ether are mixed, a small but distinct rise of temperature takes place, whereas in cases of pure admixture (such as that of ethyl alcohol and methyl alcohol) no heat-effect can be observed.

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[1] S. Young, "Fractional Distillation" (Macmillan), p. 40. See also J. Walker, *Brit. Assoc. Rep.* 18 (1911), 349.

Of the eighty-six elements, all except about seventeen are known as **metals.** Metals possess a peculiar lustre, an opacity to light, and a high conductivity for heat and electricity—properties which are, for the most part, not possessed by the non-metallic elements. Metals differ very remarkably from non-metals in their chemical, and even more in their electrochemical properties. The distinction between metals and non-metals is, however, not a sharp one; certain elements, such as iodine and tellurium—which in this book are treated as non-metals—have considerable claims to the title of metal.

The Laws of Combinations and the Atomic Theory. A most important characteristic of the simpler chemical compounds is their fixity of composition. For instance, sodium chloride, however prepared, always contains sodium and chlorine in the proportions 23 : 35·46. If a larger quantity of either constituent is present before combination occurs, the excess remains uncombined after the reaction. There are many classes of substance, for instance mixed crystals, in which the fixity of composition appears to be absent; but, in spite of these apparent exceptions, the "**Law of Definite Proportions**" remains the basis of all quantitative chemical study.

The proportions in which the elements combine display certain regularities which can scarcely be fortuitous. Two compounds of copper and oxygen are known. In one of these, cupric oxide, the elements are present in the proportions 63·57 : 16·00; in the other, cuprous oxide, they are present in proportions 127·14 : 16·00. Thus cuprous oxide contains exactly twice as much copper as does cupric oxide. This is only one single example of the very general "**law of multiple proportions.**"

Even more suggestive is the "**law of reciprocal proportions.**" Sodium and chlorine combine, as stated above, in proportions 23 : 35·46. Sodium and iodine also combine, in proportions 23 : 126·9, forming a compound known as sodium iodide. Now it happens that chlorine and iodine themselves unite to form the compound iodine chloride; and if iodine chloride be analysed the two elements are found to be present in the proportions 35·46 : 126·9.

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[1] F. Dolezalek and A. Schulze, *Zeitsch. Phys. Chem.* **83** (1913) 45.

The conclusion is almost irrestible that sodium, chlorine and iodine exist in nature, so to speak, "done up in bundles," whose weights are in some such ratio as 23 : 35·46 : 126·9. Dalton's **Atomic Hypothesis** puts the idea into definite form. According to this hypothesis all substances are supposed to consist of minute particles or atoms. The relative weight of the atoms of the substances mentioned above are supposed to be sodium 23, chlorine 35·46, iodine 126·9, oxygen 16·00, copper 63·57. Of the two compounds formed by oxygen and copper, cupric oxide is supposed to consist of oxygen and copper atoms in equal numbers, whilst cuprous oxide is believed to contain twice as many copper atoms as oxygen atoms. Expressing the copper atom by the symbol Cu, and the oxygen atom by O, we can represent cuprous oxide by the formula Cu_2O, and cupric oxide by the formula CuO.

Some years ago it was customary to take the weight of the hydrogen atom, the lightest of all atoms, as unity, and to express other atoms as multiples of it; upon such a scale the atomic weight of oxygen is approximately 15·9. It is now considered more convenient to take the oxygen atom as exactly 16·000, and when this is adopted as a standard for the atomic weights of all other elements, the atomic weight of hydrogen becomes 1·008. The following table shows the *mean* atomic weights of the elements, together with the symbol used in chemical formulæ to express an atom of any given element. It is now fairly certain that the elements whose atomic weights are not approximately equal to whole numbers consist of atoms of at least two different sizes; chlorine, for instance, probably consists of two sorts of atoms having weights 35·00 and 37·00 respectively, but they are mixed in such proportions that the average weight of the atoms in the mixture is 35·46. The two sorts of atoms have identical chemical properties, and only differ in mass.[1] This matter will be referred to again in the chapter on radioactivity.

In the middle of the last century much confusion was caused because in some cases multiples or submultiples of the present atomic weights were regarded as the true values. For instance, the atomic weight of carbon was considered by some chemists as 6·0, and the formula of methane was expressed as C_2H_4; at the present day it is believed that the atomic weight of carbon is 12·0, and we write methane as CH_4. The two views lead to exactly the same results for the quantitative composition of methane.

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[1] F. W. Aston, *Phil. Mag.* 39 (1920), 611.

International Atomic Weights (1921).

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminium	Al	27·1	Neodymium	Nd	144·3
Antimony	Sb	120·2	Neon	Ne	20·2
Argon	A	39·9	Nickel	Ni	58·68
Arsenic	As	74·96	Niton (radium emanation)	Nt	222·4
Barium	Ba	137·37	Nitrogen	N	14·008
Bismuth	Bi	208·0	Osmium	Os	190·9
Boron	B	10·9	Oxygen	O	16·00
Bromine	Br	79·92	Palladium	Pd	106·7
Cadmium	Cd	112·40	Phosphorus	P	31·04
Cæsium	Cs	132·81	Platinum	Pt	195·2
Calcium	Ca	40·07	Potassium	K	39·10
Carbon	C	12·005	Praseodymium	Pr	140·9
Cerium	Ce	140·25	Radium	Ra	226·0
Chlorine	Cl	35·46	Rhodium	Rh	102·9
Chromium	Cr	52·0	Rubidium	Rb	85·45
Cobalt	Co	58·97	Ruthenium	Ru	101·7
Columbium	Cb	93·1	Samarium	Sa	150·4
Copper	Cu	63·57	Scandium	Sc	45·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	167·7	Silicon	Si	28·3
Europium	Eu	152·0	Silver	Ag	107·88
Fluorine	F	19·0	Sodium	Na	23·00
Gadolinium	Gd	157·3	Strontium	Sr	87·63
Gallium	Ga	70·1	Sulphur	S	32·06
Germanium	Ge	72·5	Tantalum	Ta	181·5
Glucinum	Gl	9·1	Tellurium	Te	127·5
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·00	Thallium	Tl	204·0
Holmium	Ho	163·5	Thorium	Th	232·15
Hydrogen	H	1·008	Thulium	Tm	168·5
Indium	In	114·8	Tin	Sn	118·7
Iodine	I	126·92	Titanium	Ti	48·1
Iridium	Ir	193·1	Tungsten	W	184·0
Iron	Fe	55·84	Uranium	U	238·2
Krypton	Kr	82·92	Vanadium	V	51·0
Lanthanum	La	139·0	Xenon	Xe	130·2
Lead	Pb	207·20	Ytterbium (Neoytterbium)	Yb	173·5
Lithium	Li	6·94	Yttrium	Yt	89·33
Lutecium	Lu	175·0	Zinc	Zn	65·37
Magnesium	Mg	24·32	Zirconium	Zr	90·6
Manganese	Mn	54·93			
Mercury	Hg	200·6			
Molybdenum	Mo	96·0			

Not given in International List.

Actinium . . 226, Polonium . . 210, Uranium x_2 . . 234

But, of the two, the older idea would require a more complicated formula for many thousands of carbon compounds, and allows a simpler formula for very few; it has consequently been abandoned. Various considerations have helped chemists to choose between alternative numbers, and Avagadro's hypothesis, which will shortly be explained, was of especial value in enabling chemists to decide upon the correct numbers to be adopted. New work continues to show that the choice has been rightly made, and, whatever modifications the Atomic Weight table of the present day may have to undergo in the future, it is very unlikely that in the years to come we shall have to substitute for the present value of the atomic weight of any element a multiple or submultiple of the numbers accepted at the present time.

The table of atomic weights shows, of course, only the relative weights of the atoms; the absolute masses and sizes of the atoms are, however, now known. The absolute mass of a hydrogen atom is $1{\cdot}66 \times 10^{-24}$ grams; that of the oxygen atom is, of course, 15·9 times as great. Small as these numbers may seem, the mass of the hydrogen atom is about 1830 times that of the electron, the so-called atom of electricity.

Proceeding, therefore, on the assumption that the numbers given in the table represent fairly accurately the relative weights of the atoms, we can go on to examine the composition of compounds. The most important compounds containing two elements (binary compounds) are formed by union of a metal with a non-metal. If the **chlorides**, formed by union of a metal with chlorine, are studied it may be noticed that, whilst sodium chloride ($NaCl$) contains equal numbers of chlorine and sodium atoms, magnesium chloride ($MgCl_2$) and aluminium chloride ($AlCl_3$) contain respectively two and three chlorine atoms for each metallic atom. This fact may be expressed by saying that the "**positive valency**" of sodium, magnesium and aluminium are respectively 1, 2 and 3. The positive valency is thus a property of a metallic atom, and is a measure of the power to engage atoms of non-metallic elements. Hydrogen, although not resembling a metal in physical properties, often resembles a metal in its power of combination, and is frequently regarded as having a positive valency of one.

Non-metallic atoms, on the other hand, are endowed with a **negative valency**, a number representing their power to engage metallic atoms. Chlorine, regarded above as the typical non-metal, has a negative valency of one. Another important non-metal, oxygen, has a negative valency of two; the "**oxides**" of sodium, magnesium and aluminium have the formulæ

$$Na_2O,\ MgO,\ Al_2O_3,$$

and therefore contain twice as many metallic atoms for the same number of non-metallic atoms as do the chlorides,

$$NaCl,\ MgCl_2,\ AlCl_3.$$

Many substances which have less strongly marked non-metallic properties than oxygen and chlorine appear to possess *both positive and negative* valencies. Sulphur, for instance, in joining with metals to form "sulphides," behaves as a non-metal with negative valency 2; thus sodium sulphide has the composition Na_2S. Sulphur also, however, combines with the typical non-metal oxygen, and in sulphur trioxide, SO_3, appears to exert a positive valency of 6.

A simple explanation of positive and negative valency will shortly be suggested.

The Periodic System. If we write out the elements in the order of their atomic weights, commencing with hydrogen and ending with uranium, it is found that periodically we meet with a sequence of elements having properties which show striking similarity—both chemical and physical—to those of elements that have gone before.

For instance, six times in the course of the elements do we come upon certain *inert gases*, having apparently no power of combination with other substances; in other words, substances of zero valency. In five cases the inert gases are followed by highly reactive substances which possess a metallic appearance, but which react with water with great violence and yield solutions having alkaline properties; each of these "*alkali-metals*" has a positive valency of one. In four cases, the inert gases are preceded by typical non-metals, which react with metals with violence forming stable crystalline salts; these non-metals, which are called *halogens*, have a negative valency of one.

Innumerable forms of the "periodic arrangement" of the elements have been suggested which lay emphasis upon the different regularities in different ways. The table given below is considered to be the most convenient for the purposes of this book.[1] The elements are arranged exactly in the order of their atomic weights except that

(1) Argon (39·9) is placed before Potassium (39·10).

(2) Cobalt (58·97) is placed before Nickel (58·68).

(3) Tellurium (127·5) is placed before Iodine (126·92).

The whole numbers placed above the symbol simply indicate the order in which the elements stand in the table. These **atomic**

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[1] Founded mainly on an arrangement given by James Walker in his "Introduction to Physical Chemistry" (Macmillan). It is somewhat similar to the forms suggested by I. D. Margary, *Phil. Mag.* **42** (1921), 287, and by F. Paneth, *Ber.* **53** (1920), 1713. Attention is called to the spiral models devised to show the periodicity of the elements by W. D. Harkins and R. E. Hall, *J. Amer. Chem. Soc.* **38** (1916), 169.

numbers,[1] as they are called, are now considered to be of eve more fundamental importance than the atomic weights. Wit the three exceptions just given the atomic number of an elemen represents the position of that element in the order of the atomi weights. For the elements between helium and chlorine th atomic number is roughly equal to half the atomic weight.[2] Thu carbon with atomic weight 12·0 stands sixth among the element in the order of atomic weights; that is, its atomic number is six.

Hydrogen, the lightest of all the elements, is shown by som chemists as falling in Group VIIB, and by others as falling in Grou IA. It has, indeed, certain properties in common with the element of each group. In the table given below, it is omitted altogether the series commencing with helium.

It will be noticed that several gaps have been left in the tables some, at least, represent elements which are still undiscovered Indeed, when the periodic arrangement was first proposed, the thre elements scandium, gallium and germanium were still unknown and in the earlier forms of the table gaps were left at these point also. It was predicted, however, that new metals would be discovered to fill the gaps, and Mendeléeff in 1871 even ventured—after consideration of the properties of the elements around th gaps—to prophesy the characteristics of the then undiscovere elements. When—later—the three elements were discovered, i was found that their properties had been foretold with considerable accuracy.

The vertical columns of the table divide the elements into sixtee natural **groups**, known as :—

Group O ;
Groups IA, IIA, IIIA, IVA, VA, VIA, VIIA ;
The "Transition Group of Elements" (sometimes calle Group VIII) ;
Groups IB, IIB, IIIB, IVB, VB, VIB, and VIIB.

All the elements which fall into a single group have a mos remarkable similarity of chemical and physical properties. It i noticed, however, that within a group the properties as a whol vary slightly and gradually as the atomic weight rises. A simila gradual change of properties is noticed as we go along a horizonta row, or "**series**," from left to right.

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[1] H. G. J. Moseley, *Phil. Mag.* **26** (1913), 1024; **27** (1914), 703. H. S Allen, *Trans. Chem. Soc.* **113** (1918), 389.

[2] A more exact connection between atomic number and atomic weigh extending also to the heavier elements is suggested by W. D. Harkins an E. D. Wilson, *J. Amer. Chem. Soc.* **37** (1915), 1367, 1383. W. D. Harkins *J. Amer. Chem. Soc.* **39** (1917), 856. R. G. Durrant, *J. Amer. Chem. So* **39** (1917), 621.

Group	A Groups.							Transition Elements.			B Groups.							Group 0 Re-peated.
0	IA	IIA	IIIA	IVA	VA	VIA	VIIA	(8)	(9)	(10)	IB	IIB	IIIB	IVB	VB	VIB	VIIB	
2 He 0	3 Li 1	4 Be 2	5 B 3											6 C +4 −4	7 N +5 −3	8 O −2	9 F −1	10 Ne 0
10 Ne 0	11 Na 1	12 Mg 2	13 Al 3											14 Si +4 − 4	15 P 5 −3	16 S +6 −2	17 Cl 7 −1	18 A 0
18 A 0	19 K 1	20 Ca 2	21 Sc 3	22 Ti (3),4	23 V 2,3,4,5	24 Cr 2,3,6	25 Mn ,3,4,6,7	26 Fe 2,3(4)(6)	27 Co 2,3(4)	28 Ni 2(3)(4)	29 Cu 1.2	30 Zn 2	31 Ga 3	32 Ge +4(−4)	33 As 3,5−3	34 Se +6 −2	35 Br 7−1	36 Kr 0
36 Kr 0	37 Rb 1	38 Sr 2	39 Y 3	40 Zr 4	41 Nb (2)(3)(4)5	42 Mo (3)(4)6	43 —	44 Ru 3,4,6,7,8	45 Rh (2)3,4	46 Pd 2,4	47 Ag 1	48 Cd (1),2	49 In 3	50 Sn 2,4(−4)	51 Sb 3,5(−3	52 Te +6 −2	53 I 7−1	54 Xe 0
54 Xe 0	55 Cs 1	56 Ba 2	57 La 3 ↓	58 Ce 3,4 ↓														
		57 to 71 RARE EARTHS La Ce Pr Nd — Sm Eu Gd Tb Ho Dy Er Tm Yb Lu (Valency 3)			73 Ta (4)5	74 W 4,6	75 —	76 Os 2,3,4,6,8	77 Ir 2,3,4	78 Pt 2,4	79 Au 1,3	80 Hg 1,2	81 Tl 1,3	82 Pb 2,(4)	83 Bi 3,5(−3)	84 Po		86 Nt 0
86 Nt 0		88 Ra 2	89 Ac 3	90 Th 4	91 (UX_2) 5	92 U 4,6												

THE PERIODIC OR NATURAL CLASSIFICATION OF THE ELEMENTS.

The numbers below the symbol for each element represent the valency usually exerted by the element in question. It will be noticed that the **maximum positive valency** of metallic elements frequently corresponds to the Roman number at the head of the group, although in the case of the highest numbers (V, VI and VII) the valency does not always reach the maximum value.

The elements which display non-metallic characters—that is, elements capable of exerting a negative valency—lie close together at the right-hand side of the table. Those which will be treated as non-metals in this book, are separated from the others by a broken line. The negative valency, which appears to be a constant number, is always equal to $8-n$, where n is the number of the group; thus the negative valency of the halogens in Group VIIB is -1, whilst that of the elements of Group VIB is -2.

The Structure of the Atom. The periodic arrangement of the elements suggests that they are not the ultimate components of matter, but that the atoms of so-called elementary substances are themselves built up on some ordered plan from even simpler material. During the present century, physicists have obtained a considerable insight into the internal structure of the atom. It is generally believed that an atom consists of a small nucleus surrounded by electrons,[1] the number of electrons being equal to the atomic number of the element; thus an atom of hydrogen has one electron that of helium two electrons, that of lithium three electrons, and so on. The sizes of the electrons and of the nucleus are both extremely small; in the case of hydrogen and helium, the nucleus is probably the smaller of the two. An electron has probably a radius of about 2×10^{-13} cm., which is about 1/50,000 of the radius of the helium atom. Since the atom as a whole is electrically neutral, we must imagine that the nucleus, if deprived of its electrons, would have a "net" positive charge equal to that of N electrons, where N is the atomic number; recent work would seem to indicate that the nucleus of many atoms also contains electrons.

Some authorities, notably Bohr, declare that the non-nuclear electrons move continuously in orbits which are approximately elliptical or circular.[2] Others, like Langmuir, consider the mean positions of the electrons as more or less fixed, the electrons being distributed about the nucleus in a number of spherical layers[3];

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[1] Sir E. Rutherford, *Phil. Mag.* **21** (1911), 669; **27** (1914), 488.

[2] N. Bohr, *Phil. Mag.* **26** (1913), 1, 476, 857. *Nature,* **107** (1921), 104. *Zeitsch. Phys.* **9** (1922), 1. Compare L. Vegard, *Phil. Mag.* **35** (1918), 293.

[3] G. N. Lewis, *J. Amer. Chem. Soc.* **38** (1916), 762. I. Langmuir, *J. Amer. Chem. Soc.* **41** (1919), 868. The last-mentioned paper is very helpful, and the reader is strongly recommended to consult it, and also that of Sir J. J. Thomson, *Phil. Mag.* **41** (1921), 510. Recent work by W. L. Bragg, R. W. James and C. H. Bosanquet, *ibid.*, **44** (1922), 433 seems to indicate that the Lewis-Langmuir model of the atom at least requires modification.

this view, it should be understood, does not preclude a certain amount of revolution or oscillation of the electrons about their mean positions. The first theory is supported by most physicists, as it offers an explanation of certain remarkable facts regarding gaseous spectra; it is now being developed to explain the chemical properties of the different elements. The second theory, however, has the support of most chemists, since it appears to give a more direct and simple explanation of the facts of chemistry, particularly the valency of the elements, and the regularities expressed in the periodic table; at the same time, it seems possible that it may be developed in such a way as to explain the facts concerning spectra also.[1] Very likely the two views are not so inconsistent with one another as is sometimes supposed.[2] Probably the facts which are of importance to the student of metals could be explained equally satisfactorily on either theory; but it will be easier for the reader to obtain a mental picture of the mechanism of chemical combination if we adopt provisionally Langmuir's conception of an atom with electrons arranged in comparatively fixed positions on spherical shells.

The nucleus and the inner electrons have comparatively little interest for the chemist. The *nucleus* is thought to be responsible for practically the whole mass of the atom; whilst in the radioactive elements it appears to be the seat of radioactive change. The *inner layers* or inner rings of electrons are active in causing the emission of the so-called "X-rays" when the substance is bombarded by cathode-ray particles; indeed, we owe our knowledge of the inner electrons mainly to this fact. They appear to contribute very little to the chemical behaviour of the atom.

It is, however, the electrons of the *outer layer* or outer ring (the so-called "**valency electrons**") which are responsible for chemical combination between the atoms and which determine the chemical character of different substances. It is believed that when a metal (possessing positive valency) combines with a non-metal (a substance possessing negative valency) the metallic atom gives up some (frequently all) of the valency electrons from its outer layer; the electrons given up pass to the non-metallic atom, and render complete the outer layer of electrons in the latter. Since, however, the metallic atom is left positively charged, there is still an electrostatic force holding the electrons to it, and this force serves to bind the two atoms together. A clear notion of positive and negative valency is thus arrived at; positive valency consists in the power to give up electrons, and negative valency in the power to absorb them. It is possible, therefore, to express the mode of combination of the chlorides and oxides of sodium, magnesium, and aluminium in this way :—

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[1] See I. Langmuir, *Phys. Rev.* **18** (1921), 104.

[2] N. R. Campbell, *Nature*, **106** (1920), 408.

$$\mathrm{Na} \dashrightarrow \mathrm{Cl} \qquad \mathrm{Cl} \dashleftarrow \mathrm{Mg} \dashrightarrow \mathrm{Cl}$$

$$\begin{tikzcd}[row sep=small, column sep=small] & & \mathrm{Cl} \\ \mathrm{Cl} & \mathrm{Al} \arrow[l, dashed] \arrow[ur] \arrow[dr] & \\ & & \mathrm{Cl} \end{tikzcd}$$

$$\mathrm{Na} \dashrightarrow \mathrm{O} \dashleftarrow \mathrm{Na} \qquad \mathrm{Mg} \rightrightarrows \mathrm{O} \qquad \mathrm{O} \leftleftarrows \mathrm{Al} \dashrightarrow \mathrm{O} \dashleftarrow \mathrm{Al} \rightrightarrows \mathrm{O}$$

The arrow indicates the direction in which an electron has passed, and denotes the electrostatic force linking the atoms together.

That the charges upon the metallic and non-metallic atoms in the compounds mentioned have a real existence is shown in "electrolysis." If sodium chloride be fused, and an E.M.F. be applied to two poles, or electrodes, immersed in it, sodium travels to the negative pole, by virtue of the positive charge and appears as metallic sodium, whilst chlorine gas is evolved at the positive electrode; a similar decomposition is brought about if a solution of sodium chloride in water is used, but here secondary reactions complicate the result.

If the view of atomic structure suggested above is considered along with the periodic table, a reason suggests itself for the different valencies of the various elements.[1]

The inert gases of the Group O have a valency nil; presumably in their atoms the outer layer of electrons is complete, stable and self-sufficing. When, however, we pass back to the group of elements that immediately precede them, the halogens, there is evidently one less electron in the outer layer. If such an atom, therefore, absorbs one electron from outside, we may expect the outer layer to become stable; the halogens, in consequence, have a negative valency of one. A chlorine atom which has absorbed an extra electron becomes identical with the argon atom as far as the outer layer is concerned. It differs from the argon atom, of course, as regards the nucleus; the chlorine atom has a nucleus with a smaller positive charge, so that when the one extra electron has been absorbed, the atom possesses, as a whole, a negative charge. Nevertheless the charged chlorine atom or *ion* possesses the same sort of stability as the argon atom; it may be said to belong to the "**inert-gas type.**"

Similarly, the elements of Group VIB (oxygen, sulphur, selenium and tellurium) require two extra electrons in the outer layer to attain to the inert gas type; these elements have a negative valency of two. The elements of Group VB have a negative valency of three; but in this group the power to absorb electrons begins to weaken, and with it the non-metallic character of the elements.

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[1] I. Langmuir, *J. Amer. Chem. Soc.* **41** (1919), 868, 1543. See also W. L. Bragg, *J. Soc. Chem. Ind.* **39** (1920), 335R.

If we pass now to Group IA, which consists of elements possessing one more electron than the inert gases, it is evident that this one electron constitutes an "extra" or "valency electron" outside the stable layer. If this electron can be passed on to another atom, the "inert type" is left. The alkali metals have therefore a positive valency of one.

In Group IIA a second valency electron is added, and we have a positive valency of two; similarly the succeeding groups IIIA, IVA, VA, VIA and VIIA have three, four, five, six, or seven valency electrons, and the maximum valency is 3, 4, 5, 6 and 7 respectively. As the number of valency electrons grows, however, it is noteworthy that the maximum valency is not always exerted. Manganese, for instance, is capable of parting with seven valency electrons, but this leaves the atom with a very strong positive charge, and it requires considerable energy to remove the last few electrons. Compounds like Mn_2O_7, in which manganese has a valency of seven, are, as a result, distinctly unstable. Metals of Groups VIA, VIIA, and the *transition elements* tend, rather, to form compounds in which the metals exert a valency of two or three; this is especially noticed in the *transition elements*, in which the full valency (8, 9 or 10) is very rarely reached.

When we come to Group IB, a new state of affairs is met with. These metals should have eleven valency electrons, but, of these, ten appear to form a "semi-stable" layer by themselves, and the metals possess a valency of one, forming compounds of the type CuCl, AgCl, AuCl. The valency is, however, not invariable, as is the case in Group IA; copper, for instance, is also divalent, forming a second chloride, $CuCl_2$. The valency of the metals of the following Groups IIB, IIIB and IVB is generally 2, 3, and 4 respectively, but here again it is often variable. When we reach Group VB, we see indications of a positive valency of 5, although the elements more commonly exert a valency of 3. At this point elements commence to absorb electrons so as to attain to the "type" of the next inert gas; consequently non-metallic characteristics begin to appear, which, as stated above, are still more marked in Groups VIB and VIIB.

Types of Chemical Combination.[1]

I. Polar Compounds. In all the compounds considered so far, the force joining the atom is apparently **electrical.** An electron passes from one atom to another, and the attraction between the two oppositely charged atoms holds them together. When an atom of sodium, possessing one electron in excess of the number needed for complete stability, joins to an atom of chlorine, which possesses one electron too few, both atoms assume the stable "inert" type, and the resultant compound, Na→Cl, is very stable. "The arrow linkage" may here be employed with success.

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[1] G. N. Lewis, *J. Amer. Chem. Soc.* **35** (1913), 1448. S. H. C. Briggs, *Trans. Chem. Soc.* **111** (1917), 253. See especially Sir J. J. Thomson, *Phil. Mag.* **27** (1914), 758.

II. **Non-polar Compounds.** Whilst the passage of an electron readily explains the union of dissimilar elements, it fails to give a satisfactory interpretation of the union of like atoms. Yet atoms of the same kind readily unite. The gaseous elements, such as hydrogen, oxygen, nitrogen and chlorine are believed to consist, not of single atoms, but of closely joined pairs of atoms. It has been suggested that the two atoms share a pair of electrons [1]; one author,[2] referring to the constitution of hydrogen, gives a picture of two electrons moving in a single circular orbit around the line joining the nuclei of the two atoms.

It is, however, quite possible that forces between two atoms of the same kind are **magnetic** in character.[3] If the electrons move rapidly in circular orbits, as is assumed in most theories, the effect is the same as that of an electric current passing round a circular loop of wire. When a current passes in the same direction through two loops of wire the loops will attract each other; similarly two atoms containing electrons moving round orbits in the same direction will attract one another. The combination of two hydrogen atoms to form a "molecule" has been elucidated in this manner.

Similar ideas have been introduced to explain the linkage of carbon atoms in organic compounds. Carbon falls in a peculiar position in the periodic table. It occupies a place half-way between two inert gases (Helium and Neon). Its positive valency and its negative valency should both be equal to four, and its capacity to give up or to absorb electrons should presumably be about equal. Possibly this is why carbon atoms have a unique power of joining, one to another, to form rings, or long chains, of great stability. It has been suggested that two carbon atoms joined together share a pair of electrons,[1] or perhaps exchange a pair of electrons. The alternative interpretation that the carbon atoms in a chain are held together by magnetic forces set up by electrons moving in circular paths is, perhaps, equally acceptable.[2]

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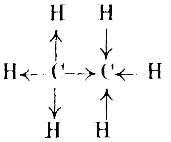
[1] J. Stark, *Jahrbuch Radioakt. Elekt.* **5** (1908), 124. See also H. Teudt, *Zeitsch. Anorg. Chem.* **106** (1919), 189.

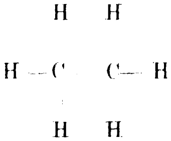
[2] N. Bohr, *Phil. Mag.* **26** (1913), 857. Compare W. A. Noyes, *J. Amer. Chem. Soc.* **39** (1917), 881.

[3] The reader is recommended to refer to a paper by A. L. Parson, *Smithson. Misc. Coll.* **65** (1915), No. 11. A paper by Sir W. Ramsay, *Proc. Roy. Soc.* **92** (A) (1916), 451, may also be profitably consulted, although his views are inconsistent with others quoted in this volume. Parson's views are also not easy to reconcile with the accepted nuclear theory of the atom, but are nevertheless worth a careful study.

Whatever view is adopted, the carbon atom appears almost invariably to possess four bonds, through which it can unite with four surrounding atoms, and these bonds are usually non-polar in character. Structural formulae such as (*a*) employing arrow-linkages do not correspond to the properties of the carbon compounds; it is best to denote the bonds around carbon atoms by plain lines, as in (*b*):—

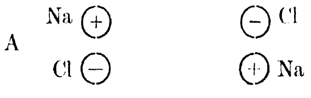
(*a*) 

$$\begin{array}{ccccc} & H & & H & \\ & \uparrow & & \downarrow & \\ H\leftarrow & C & \rightarrow & C & \leftarrow H \\ & \downarrow & & \uparrow & \\ & H & & H & \end{array}$$

(*b*) 

$$\begin{array}{cccc} & H & H & \\ H- & C & C & -H \\ & H & H & \end{array}$$

III. Molecular Compounds. Even when two or more atoms have united by polar bonds to form a compound in which the maximum valency is exerted, their power of combination is not necessarily exhausted.[3] Consider, for instance, a sodium and chlorine atom in close union, the former bearing a positive charge, the latter a negative charge; we may term the pair a "molecule" of sodium chloride. The force exerted by one such molecule, A, upon another similar molecule, B, is, at any great distance, very small; for any force exerted by the positively charged sodium atom in A is roughly compensated by the opposite force exerted by the negatively charged chlorine. If, however, the second molecule, B, approaches so near to A that the distance between the two atoms within each molecule is no longer insignificant compared to the distance separating the molecules, the force between the molecules becomes appreciable. Should the molecules approach in the way shown below, the distance separating the unlike atoms of A and B being less than that separating the like atoms, the attraction will exceed the repulsion:—



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[1] Sir J. J. Thomson, *Phil. Mag.* **27** (1914), 784. See also W. D. Harkins and H. H. King, *J. Amer. Chem. Soc.* **41** (1919), p. 976, with special reference to the footnote.

[2] A. E. Lacomblé, *Chem. Weekblad.* **16** (1919), 832.

[3] Sir J. J. Thomson, *Phil. Mag.* **27** (1914), 758. I. Langmuir, *J. Amer. Chem. Soc.* **38** (1916), 2221. W. D. Harkins and H. H. King, *J. Amer. Chem. Soc.* **41** (1919), 970. See also J. Stark, *Jahrbuch Radioakt. Elekt.* **5** (1908), 135.

In such a case there will be a resultant attractive force between the two molecules. Thus it happens that groups of atoms, in which the ordinary valency is apparently fully exerted, may nevertheless cluster together owing to these intermolecular forces. Clustering of that kind is responsible for the condensation of gases to form liquids and solids; the intermolecular forces are in such cases represented by the so-called "physical forces" of cohesion and surface tension. There is, however, no sharp distinction between physical and chemical forces and the attraction between apparently stable molecules leads also to unexpected chemical combination between substances which might well have been regarded as inert. As has already been pointed out the admixture of chloroform and ether leads to a considerable rise of temperature, which points to chemical interaction between the substances. In this instance, a definite compound, $(C_2H_5)_2O.CHCl_3$, has been isolated in the solid state by cooling the mixture. Numerous other examples of molecular compounds are known.

Importance of Spatial Considerations in determining the Possibility of the Existence of Compounds. The formation of molecular compounds—like the formation of liquids and solids—is mainly confined to low temperatures; at low temperatures the thermal agitation of the molecules is least, and consequently the molecules are less likely to be swept away from each other to distances at which intermolecular forces cease to operate.

In the solid state, in fact, the thermal agitation is so slight that comparatively small forces between atoms are sufficient to hold them together. It seems likely that there would be no limit to the number of compounds which could exist in the solid state, if it were not for another factor which here comes into play; the possibility of existence of any definite compound must depend upon whether the relative sizes of the atoms permit of them to be packed together in such a way as to produce a stable crystal structure. The chemistry of solid compounds is therefore rather a matter of geometry than of dynamics.[1]

There occur, for instance, among the constituents of alloys, solid **intermetallic compounds**,[2] such as $NaHg_2$, $AuMg_2$, Au_2Mg_5, $AuMg_3$, the composition of which has no relation to the valency of either metals. Except in certain intermetallic compounds containing arsenic, antimony and bismuth, such as As_2Fe_3, K_3Bi, $SbCu_3$ (in which arsenic, antimony, and bismuth really behave as non-metals and exert their normal negative valency of three), the law of valency appears to give no assistance in determining whether a compound of a given formula is capable of existence or not. Why, for instance, can $AuMg_2$ and $AuMg_3$ exist, and not Au_2Mg ? No definite answer can be given at present, but it is probable that the explanation, when available, will be concerned largely with the relative sizes of the magnesium and gold atoms.

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[1] Compare R. B. Sosman, *J. Ind. Eng. Chem.* 8 (1916), 989.

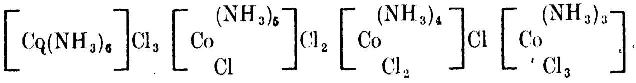
[2] A general account of these bodies is given by C. H. Desch in "Intermetallic Compounds" (Longmans, Green & Co.).

Solid substances crystallizing from solution generally possess the composition demanded by the laws of valency simply because they could not otherwise have existed in the solution. Nevertheless the crystals produced frequently contain a large proportion of solvent ("water of crystallization," for instance) which plays an essential part in the crystal structure.[1] And, if the solution contains two salts, they may combine to produce a crystalline double salt of very stable character, the existence of which would be difficult to account for on the simple electronic theory of valency. A good example is carnallite, $KCl.MgCl_2.6H_2O$.

Spatial considerations enter largely into one important class of compounds which can exist not only in the solid state but also in solution. The atom of each of the "Transition Elements" (iron, cobalt, nickel, etc.) possesses a peculiar power of attracting six atoms or atomic groups (for instance, NH_3) into very close union with itself. Apparently the six atoms or atomic groups form a very stable ring or shell round the metallic atom. The formation of the "group of six" does not interfere with the exercise of ordinary polar valency. The metal will still, for instance, combine with three atoms of chlorine, but, if any of these three chlorine atoms form part of the group of six, they are much more closely bound to the metal than is the chlorine of sodium chloride. Cobalt chloride forms the following compounds with ammonia (NH_3) :—

$$CoCl_3.6NH_3 \quad CoCl_3.5NH_3 \quad CoCl_3.4NH_3 \quad CoCl_3.3NH_3.$$

These are generally expressed in such a way as to show the group of six intimately joined members within a square bracket, thus[2] :—



$$\left[Co(NH_3)_6\right]Cl_3 \quad \left[Co\begin{matrix}(NH_3)_5\\ \\ Cl\end{matrix}\right]Cl_2 \quad \left[Co\begin{matrix}(NH_3)_4\\ \\ Cl_2\end{matrix}\right]Cl \quad \left[Co\begin{matrix}(NH_3)_3\\ \\ Cl_3\end{matrix}\right].$$

Of the four compounds, the first resembles sodium chloride in that all the chlorine can easily be separated by means of reagents, such as silver nitrate; in the second, two-thirds of the chlorine can be removed by silver nitrate or by acids at low temperatures, but the remaining chlorine atom—which forms part of the stable

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[1] L. Vegard and Schjelderup, *Ann. Phys.* **54** (1917), 146. L. Vegard, *Ann. Phys.* **63** (1920), 753.

[2] See A. Werner, *Ber.* **40** (1907), 15

"group of six "— is only rendered reactive by boiling the solution, an operation which breaks up the whole compound. The third compound has only one-third of the chlorine in a readily active condition. Solutions of the last compound—in which all the chlorine is believed to form part of the "group of six"—should, properly speaking, show none of the reactions of a chloride; this is not quite true because it is in part broken up by water, but the general chemical behaviour of the compound, which is very inert, supports the view that the whole of the chlorine is required for the formation of the complex.

Six is said to be the "**co-ordination number**" of these compounds. The formation of the stable group or ring is possibly connected with the low atomic volume of the "transition elements"; the groups probably come close enough to the nucleus to be attracted by the positive charge upon it. The metals which lie, in the Periodic Table, on either side of the transition elements, chromium, copper and the like, have also fairly low atomic volumes; these metals form similar compounds, in which the co-ordination number of six appears. The co-ordination number thus seems to be independent of the polar valency of the metal, and of the general character of the atoms attracted; it is probably determined by the geometrical arrangement of atoms around the metal. It is thought that they are arranged at the six corners of an octahedron, at the centre of which is the metallic atom.

Compounds with co-ordination numbers of four and eight have also been described; they are less stable than those having a co-ordination number of six.

III. The States of Matter

All substances exist in the **gaseous** state at very high temperatures, and in the **crystalline** (solid) state at very low temperatures; at intermediate temperatures, a **liquid** state is generally capable of existence, whilst it is often possible to produce a **glassy** or **amorphous solid** state by cooling a liquid very quickly. The glassy condition, although conferring the rigidity of crystalline solids, has probably a closer connection with the liquid state. The different states of matter can now be studied in detail.

The Gaseous State. The two most striking properties of the gases are: firstly, their extreme lightness; secondly, their compressibility and power of expansion. The smallest quantity of gas will fill completely the whole volume of any vessel into which it is introduced; but, if pressure be applied to it, the volume will decrease. To a first approximation, the volume is inversely proportional to the pressure applied to it. Gases expand considerably when heated, the volume being approximately proportional to the "absolute temperature." We can express these approximate laws by the equation:-

$$PV = RT,$$

where P is the pressure
V is the volume of the gas
T the "absolute temperature"[1]
and R a constant.

The properties of gases are satisfactorily explained by the so-called "kinetic theory." According to that theory, gases consist of minute "molecules" separated from each other by distances which are very large compared to the diameters of the molecules themselves; these molecules are in a condition of rapid motion ("thermal agitation"), which becomes greater as the temperature becomes higher. The motion of the molecules accounts for the expansion of a small amount of gas to fill any vessel into which it is introduced, whilst the bombardment of the sides of the vessel by the molecules, which rebound after impact, represents the pressure exerted by the gas.

As a result of the rapid movement, two molecules will often collide together; normally they will rebound away from each other almost immediately. Occasionally, however (especially if the temperature be low and the velocity of the molecules correspondingly small), two colliding molecules may remain in proximity for an appreciable time, and in some cases attractive forces may cause more or less permanent union between them.

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[1] The "absolute temperature" is obtained approximately by adding 273° to the temperature on the Centigrade scale; "absolute zero" is −**273° C.**

In the case of the alkali metals, which become gaseous at high temperatures, the molecules consist of single atoms; such gases are highly reactive. In non-metals—such as oxygen, hydrogen and nitrogen—which are gaseous at ordinary temperatures, the molecule consists of a pair of atoms, bound together presumably by non-polar linkage; these gases are, therefore, usually written O_2, H_2, N_2. Such gases show comparatively little chemical activity—a circumstance which is in part due to the fact that each of the molecules consists of a pair of atoms. For instance, oxygen and hydrogen can exist together at ordinary temperatures indefinitely without combining, although, if the mixture is heated, combination occurs with great violence, water vapour (H_2O) being produced. Presumably the molecule which is so stable at ordinary temperatures becomes less stable as the temperature is raised.

Where it is possible to obtain oxygen, hydrogen, or nitrogen in the state of single atoms, they are highly reactive bodies; for instance, oxygen and hydrogen gases at the moment of liberation display unusual activity, and are referred to as "nascent oxygen" and "nascent hydrogen."

The molecules of compound substances in the gaseous state can now be considered. Sodium chloride passes into a state of vapour at high temperatures and each molecule appears to consist of a single sodium atom joined to a single chlorine atom, thus:—

$$NaCl.$$

On the other hand, the molecules of aluminium chloride, in the vapour state, have not, at temperatures below 400°, the simplest formula $AlCl_3$. Some consist of a pair of simple molecules held together by intermolecular forces; such double molecules can be written

$$Al_2Cl_6.$$

At higher temperatures the proportion of simple $AlCl_3$ molecules increases, and above 750° practically all the molecules are of this simpler character.[1]

Owing to the comparatively great distance separating one molecule from the next in the gaseous state, the term "molecule" has a very definite meaning in the case of gases—a meaning which becomes somewhat shadowy in liquids and solids.

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[1] L. F. Nilson and O. Petterson, *Zeitsch. Phys. Chem.* 1 (1887), 459; (1889), 206.

It is only possible to refer briefly to **Avagadro's Hypothesis,** although our choice of consistent atomic weights for the elements, as well as all our knowledge of the complexity of gases, is based upon it. The hypothesis states that "equal volumes of gases—at corresponding temperatures and pressures,—contain equal numbers of molecules." It follows that the **molecular weight** of a substance—the weight of a single molecule referred to a hydrogen atom as unity—is proportional to the **density** of the gas, the weight of unit volume. The densities of gaseous substances can be found experimentally, and can conveniently be expressed as multiples of the density of hydrogen. The molecular weight of hydrogen (H_2) is approximately 2, and the approximate molecular weights of other substances can therefore be obtained by doubling the density number. It is by determinations of "vapour density" that we know that the molecule of gaseous sodium chloride is NaCl, whilst that of aluminium chloride, below 400°, is Al_2Cl_6.

The Liquid State. Imagine a quantity of gaseous sodium chloride cooled slowly from a very high temperature. As the temperature drops, the molecular velocity becomes smaller; accordingly, the chance of any two colliding molecules remaining bound together by intermolecular forces for an appreciable time increases. At first it may happen that two NaCl molecules merely remain in union for an instant, and part again before a third one comes up. But, as the temperature falls farther, the clustering capacity of the molecules will increase, and molecules will join up with one another more quickly than they break away. The original group of two or three molecules may then increase until it becomes a veritable swarm. In other words, the gas begins to condense to form drops of **liquid.**

In the liquid state each molecule is so near to its neighbour that it always keeps within the range of intermolecular attraction; consequently liquids are very much more dense than gases. Moreover the comparatively small distance between the molecules renders liquids almost incompressible. When a vessel filled with gas is cooled down until the gas is partially condensed, the swarm of mutually-bound molecules which forms the liquid occupies only a certain definite volume, and consequently only fills the lowest part of the vessel which originally contained the gas. A sharp boundary exists between the dense liquid below and the remainder of the vaporous substance above, and it is the existence of this sharp boundary which is especially characteristic of liquids. For the molecules at the surface of a liquid are in different circumstances to those of the interior. The latter are, on the average, equally attracted in all directions. But the surface molecules experience less attraction in one direction—namely, across the surface—than in any other. The absence of forces acting upon the surface molecules in a direction normal to the surface is accompanied by a powerful attractive force acting between the molecules in a direction parallel to the surface; consequently liquids behave as though they were enclosed by an elastic membrane, which tends to contract and thus to reduce the free surface of the liquid to a minimum. The surface area of a given volume of liquid reaches a minimum if the liquid assumes a spherical shape, and the tendency of mercury and other liquids to form spherical globules is the outcome of this contractile force, which is known as **surface tension.**

Where two immiscible liquids come into contact a similar contractile force is found at the interface, the magnitude of the force depending on the character of both liquids; this is known as "**interfacial tension.**" When two such liquids are shaken up together, one liquid becomes dispersed in the other as globules, which possess an approximately spherical form. In general, however, the small globules tend to unite together when they come into contact, the total area of contact between the two liquids being reduced by such union. Finally the liquids usually separate into two layers.

Although the velocity of the molecules in the liquid state is less than that of the gaseous molecules, the agitation still continues, the molecules moving relatively to one another. Consequently a liquid lacks rigidity, and will usually subside under the influence of gravity to assume the shape of the lower part of any vessel into which it is poured, the shape being sometimes modified, especially at the edges of the free surface, by the force of surface tension, mentioned above. As the temperature falls farther, however, and the molecular motion becomes less rapid, the rate at which the liquid changes its shape under the influence of forces such as gravity becomes smaller. The liquid acquires a "treacly" character and is said to possess a high "viscosity."

Since, in the liquid state, the molecules are practically contiguous, it may be difficult to say precisely where one molecule ends and another begins. Consequently, although the term "molecule" can still be usefully employed in dealing with the liquid state, it has not that exact meaning which it possesses where the gaseous state is concerned.

The Crystalline State. So long as the sodium chloride remains liquid, the whole mass is without rigidity or definite structure. It would be reasonable to suppose that there must be some definite geometrical arrangement of the atoms throughout the whole mass which would be more stable than any other. Whilst the temperature remains elevated, the thermal movement of the molecules relatively to one another creates too great a disturbance for the attainment of that stable arrangement. But, as the liquid cools, a temperature is reached (the "freezing-point") at which the salt begins to "crystallize" at one or more points, and the crystallization spreads out from these points until the whole mass is solid. The substance has now acquired **rigidity**—it will retain its form even after removal from the containing vessel.

If the crystalline substance is again heated, it "melts," returning to the liquid condition. In a pure substance, the "melting-point" should be identical with the true "freezing-point." It is often possible to cool a molten substance below the true freezing-point without solidification commencing, but the "*super-cooled*" liquid is in a "*metastable*" condition, and will commence to crystallize at once if a minute crystal of the solid substance is added as a nucleus. The "freezing-point" or "melting-point" can be defined as the temperature at which solid and liquid are in equilibrium.

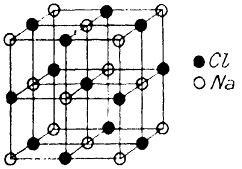

Fig. 6.

The remarkable application of the X-rays to the problems of crystal structure[1] has actually led to the discovery of the probable arrangement of atoms in a crystal of sodium chloride. If we can imagine the crystal divided into minute cubes (the length of the side of each cube being $2{\cdot}8 \times 10^{-8}$ cms.), the centres of the sodium and chlorine atoms will be placed alternately at the corners of the cubes, as is shown in Fig. 6. Each sodium atom is equidistant from six chlorine atoms; each chlorine atom is equidistant from six sodium atoms. Probably each sodium atom has lost an electron and is therefore positively charged, whilst each chlorine atom has gained an electron and is negatively charged. Any given atom is nearer to the "unlike" atoms which should attract it than to "like" atoms which would repel it; probably it is this last fact which accounts for the stability of the structure.[2] At all events, the structure is so stable that the crystalline salt possesses rigidity. This does not mean that all thermal agitation has ceased in the crystalline state. The atoms continue to move, but, so long as the temperature is below the melting-point, their range of movement is limited, and they merely oscillate about the mean positions shown in Fig. 6; the crystal-structure is thus preserved in spite of the thermal movement.

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[1] W. H. & W. L. Bragg, *Proc. Roy. Soc.* 88 [A] (1913), 428; 89 [A] (1914), 248, 277, 468. A short and simple account of the work is given by W. H Bragg, *Trans. Chem. Soc.* 109 (1916), 252.

[2] See W. L. Bragg, *Phil. Mag.* 40 (1920), 183.

The "identity of the molecule"[1] may be said to vanish completely when sodium chloride crystallizes. Each sodium atom is surrounded by six chlorine atoms; but no one of these appears to have closer claims to be regarded as its special partner than any other. If the word "molecule" has any meaning at all, the whole crystal must be regarded as a single molecule. It is true that a salt like sodium chloride represents an extreme example of the inapplicability of the term "molecule" to the case of crystalline substances. Further work may prove that in some solid substances there exist groups of atoms which are specially closely related together. There is already evidence that this may be true of organic compounds, which it should be noted, are in general much more "compressible" than inorganic compounds—a fact which is no doubt connected with the presence of "voids" between the different molecules.[2] The latest X-ray investigations of the crystal-structure of such organic compounds as naphthalene[3] certainly seem to show that it is legitimate to employ the word "molecule" for the groups of closely related atoms in solid *organic* bodies; but, in most *inorganic* compounds, it is probably incorrect to speak of "molecules" as persisting in the solid state.

The structure of sodium chloride sketched in Fig. 6 shows that the atoms are arranged in layers situated along parallel planes. It is not surprising to find that the crystal breaks along these planes ("cleavage planes") more easily than in other directions. If a large crystal of sodium chloride is broken up the pieces will be found to be bounded by three planes at right angles, and often approximate in shape to small cubes.

In fact, crystals may be said to differ from liquids and from glasses mainly in possessing "different properties in different directions"; the systematic arrangement of the atoms in crystals—as opposed to the chaotic arrangement in liquids and glasses—readily accounts for this distinction. Some classes of crystals are found to have varying conductive powers for heat or for electricity, according to the direction in which they are tested. Very commonly the optical properties vary according to the direction in which the light passes through the crystals; occasionally, the crystal appears to have one colour if viewed in one direction and a different colour when it is viewed in another direction. Even the chemical activity of crystals appears to vary with the direction; a corrosive acid, acting upon a crystalline grain of metal, dissolves it more quickly in some directions than it does in others. The "etching-pit" produced has, therefore, an outline—often that of a cube or octahedron—which is closely related to the internal arrangement of the atoms.

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[1] A. H. Compton, *J. Franklin Inst.* **185** (1918), 745. I. Langmuir, *J. Amer. Chem. Soc.* **38** (1916), 2221.

[2] See A. Reis, *Zeitsch. Phys.* **1** (1920), 204.

[3] Sir W. H. Bragg, *Proc. Phys. Soc.* **34** (1921), 33.

One of the most important peculiarities of the crystalline state is displayed by the fact that a freely growing crystal usually assumes a definite geometrical form. Freedom of growth is essential in order to obtain this form. If a quantity of sodium chloride is fused and allowed to solidify in a vessel, the resultant crystalline mass will obviously have the form of the containing vessel. If, however, a crystal of sodium chloride be grown from aqueous solution, out of contact with the sides of the vessel or with other crystals, it will be found to have a cubic form; and, when we recollect the arrangement of sodium and chlorine atoms in the crystals, the appearance of a cubical outline is by no means surprising.

Whilst sodium chloride usually—although not always—appears in cubes, other substances crystallize in other forms. In practically all cases, however, the arrangement of the plane faces that bound the crystals is not haphazard, but represents some definite rule of symmetry. Faces may occur in pairs parallel to one another on opposite sides of the crystal (**centro-symmetry**). Or they may fall into pairs, on opposite sides of a "**plane of symmetry**," and making equal angles with it. Lastly, the faces may occur in sets of two, three, four, or six, symmetrically arranged around a diad, triad, tetrad, or hexad "**axis of symmetry**" and making equal angles with it. In any case, *the symmetrical occurrence of the faces is merely an outward sign of the systematic arrangement of the atoms throughout the crystal.*

According to the degree of symmetry present, crystals may be divided into thirty-two classes, which are conveniently grouped into six main systems.[1] Only one class consists of crystals devoid of all symmetry. For purposes of reference the elements of symmetry corresponding to the different classes is given in the table on page 42; but to those unacquainted with crystallography the table will convey but little, and consequently a few of the commoner forms of crystals—met with in the six systems—are shown in Fig. 7.

The crystals shown in Fig. 7 are assumed to have grown under

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[1] The symmetry of the different classes of crystals is well described by A. E. H. Tutton in his "Crystallography and Practical Crystal Measurement" (Macmillan).

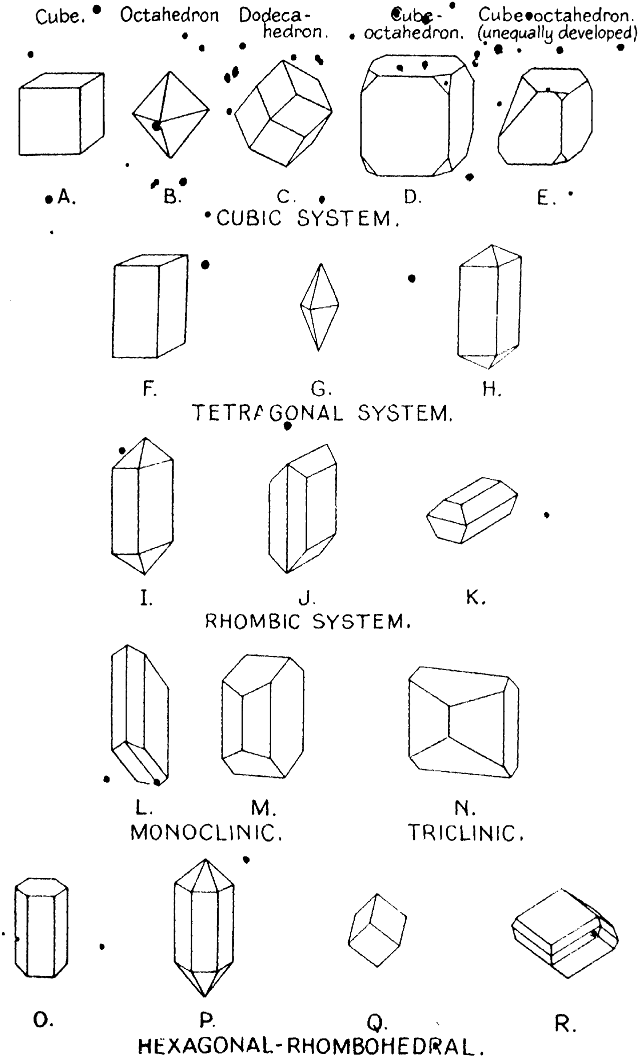


FIG. 7.

unusually favourable conditions; corresponding faces are shown as equally developed. The only exception is Fig. 7E, which

System.	Class	Elements of Symmetry.	Example of Substance Crystallizing in Class.
Anorthi	(1)	No symmetry	Calcium thiosulphate
	(2)	Centro-symmetry	Copper sulphate
Monoclinic	(3)	1 Diad Axis	Potassium tetrathionate
	(4)	1 Plane of Symmetry	Cane sugar
	(5)	1 Plane of Symmetry; 1 Diad Axis; Centro-Symmetry	Gypsum (hydrated calcium sulphate)
Rhombic	(6)	3 Diad Axes at right-angles	Zinc sulphate
	(7)	3 Diad Axes; 3 Planes of Symmetry; Centro-Symmetry	Barium sulphate
	(8)	1 Diad Axis, the intersection of 2 Planes of Symmetry at right-angles	Smithsonite (basic zinc silicate)
Tetragonal	(9)	1 Tetrad Axis	Wulfenite (lead molybdate)
	(10)	1 Tetrad Axis; 1 Plane of Symmetry at right-angles to it; Centro-Symmetry	Scheelite (calcium tungstate)
	(11)	1 Tetrad Axis; 4 Diad Axes at right-angles to it	Strychnine sulphate
	(12)	1 Tetrad Axis; 4 Planes of Symmetry meeting in it	Silver fluoride
	(13)	1 Tetrad Axis; 4 Diad Axes; 5 Planes of Symmetry; Centro-Symmetry	Cassiterite (tin oxide)
	(14)	3 Diad Axes, one being the intersection of 2 Planes of Symmetry at right-angles	Copper pyrites ($CuFeS_2$)
	(15)	"Pseudotetrad" Diad Axis (no substance crystallizes in this system, hence no further explanation need be given)	(None known)
Cubic	(16)	4 Triad Axes; 3 Diad Axes	Barium nitrate
	(17)	4 Triad Axes; 3 Diad Axes; 3 Planes of Symmetry; Centro-Symmetry	Iron pyrites (FeS_2)
	(18)	4 Triad Axes; 3 Tetrad Axes; 6 Diad Axes	Sodium chloride
	(19)	4 Triad Axes; 3 Tetrad Axes; 6 Diad Axes; 9 Planes of Symmetry; Centro-Symmetry	Metallic silver
	(20)	4 Triad Axes; 3 Diad Axes; 6 Planes of Symmetry	Blende (zinc sulphide)
Hexagonal-Rhombohedral A. Rhombohedral	(21)	1 Triad Axis	Sodium periodate
	(22)	1 Triad Axis; Centro-Symmetry	Phenakite (beryllium silicate)
	(23)	1 Triad Axis; Plane of Symmetry at right-angles	(None known)
	(24)	1 Triad Axis; the intersection of 3 Planes of Symmetry	Greenockite (cadmium sulphide)
	(25)	1 Triad Axis; the intersection of 3 Planes of Symmetry. A fourth Plane of Symmetry at right angles to it; 3 Diad Axes.	(None known)
	(26)	1 Triad Axis; 3 Diad Axes at right angles to it.	Quartz (silica)
	(27)	1 Triad Axis; 3 Diad Axes at right angles to it; 3 Planes of Symmetry; Centro-Symmetry	Calcite (calcium carbonate)
B. Hexagonal	(28)	1 Hexad Axis	Lithium potassium sulphate
	(29)	1 Hexad Axis; 1 Plane of Symmetry at right-angles to it; Centro-Symmetry	Apatite
	(30)	1 Hexad Axis; 6 Planes of Symmetry	Silver iodide (probably)
	(31)	1 Hexad Axis; 6 Planes of Symmetry; Centro-Symmetry	Beryl
	(32)	1 Hexad Axis; 6 Diad Axes at right-angles to it	Double salt of lead antimony tartrate and potassium nitrate

represents a crystal grown under conditions more favourable for the development of some faces than of others. As a result, the crystal has an ill-shaped appearance, but, nevertheless, it obeys the laws of crystal symmetry, just as well as the evenly-developed crystal 7D, with which it is crystallographically identical. For the laws of crystal symmetry merely govern the angles which the various faces make with the planes and axes of symmetry, and do not determine the size of the individual faces.

Of considerable importance in crystallography is the occurrence of compound crystals, or **twins**. An example is shown in Fig. 8. Here we see a twin crystal of gypsum, consisting of two single crystals arranged symmetrically on either side of a **twinning-plane**. The twinning-plane is invariably parallel to a possible face of the crystal, but is never parallel to a plane of symmetry of the single crystal. This kind of twinned crystal has frequently a re-entrant angle on one side, and is sometimes known as the "arrow-head twin." The re-entrant angle and general appearance aid the observer to recognize the combination as a twin. Other types of twins, however (including those in which there is a twin-axis, instead of a twinning-plane), are more difficult to recognize; and in many cases the earlier crystallographers were led to regard what was really a twinned crystal of a substance crystallizing in a class of low symmetry as a single crystal belonging to a class of higher symmetry.

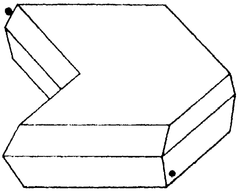


FIG. 8.

Many substances including some rock-forming minerals, such as plagioclase felspar are found built up of innumerable thin parallel **twin-lamellæ**. The planes separating the lamellæ act as twinning-planes, and the material is orientated differently in alternate lamellæ. No doubt the layers of atoms on each side of a twinning-plane make equal angles with it, possibly in the manner suggested in Fig. 9. The edge of a crystal made up of twin-lamellæ, viewed in the correct light, will often show a series of striæ, due to reflection from the parallel facets *a*, *a*, *a*, or, alternatively, from the series *b*, *b*, *b* (Fig. 9).

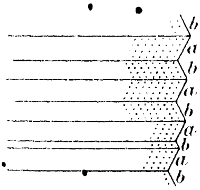
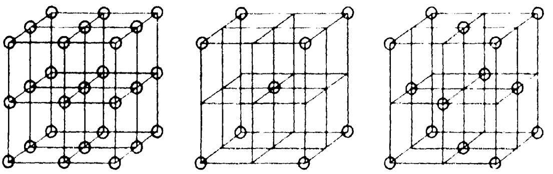


FIG. 9.

Twinned crystals of a similar character occur also in metals which have been mechanically strained, as will be shown in Chapter II of this volume.

Crystal-Structure of Metals. Whilst the symmetry and crystal habit of all common substances have long been known, and the characteristic angles between faces have been measured with great accuracy, the internal arrangement of atoms, which give rise to the symmetry, is only known for a comparatively few compounds. In the example which has been considered above, sodium chloride, the arrangement of atoms is extremely simple. Many other binary compounds have a similar internal structure. But most compounds containing more than two elements have a far more complicated arrangement of the component atoms, and it is often difficult to describe it without the aid of models.[1]

For the purpose of this book the crystal-structure of the metals in the uncombined state possesses special importance. Most of the commoner metals crystallize in the cubic system. There are three important ways of arranging the atoms which would give the necessary symmetry of the cubic system. We may imagine space divided into minute cubes of equal size, and then picture the atoms arranged with their centres at the corners of the cubes; this arrangement is represented by the **simple cubic space-lattice** (Fig. 10A). Again, we can imagine an atom at the corner and also at the centre of each cube, as is represented by the **centred cube space-lattice**[2] (Fig. 10B). Thirdly, we can picture the atoms placed at the corners of the cubes and also at the centres of the faces; such an arrangement is represented by the **face-centred cubic space-lattice** (Fig. 10C).



A B C

FIG. 10.

Now, of the common metals which belong to the cubic system it has been found that[3]:—

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[1] The structure of several compounds is discussed by W. H. and W. L. Bragg in their book on "X-rays and Crystal Structure" (Bell).

[2] Often called the body-centred cubic lattice to distinguish it from the face-centred cubic lattice.

[3] W. H. Bragg, *Phil. Mag.* **28** (1914), 355; *Trans. Chem. Soc.* **109** (1916), 252. A. W. Hull, *Phys. Rev.* **10** (1917), 661; *Trans. Amer. Inst. Electr. Eng.* **38** (1919), 1445; *Science*, **52** (1920), 227. P. Scherrer, *Phys. Zeitsch.* **19** (1918), 23. L. Vegard, *Phil. Mag.* **31** (1916), 83; **32** (1916), 65. P. Debye, *Phys. Zeitsch.* **18** (1917), 483.

Iron, Chromium, Molybdenum, Tungsten, Sodium and **Lithium** have their atoms arranged on a **centred-cubic space-lattice** (Fig. 10B).

Copper, Silver, Gold, Aluminium, Lead, Rhodium, Platinum, Cobalt and **Nickel** have their atoms arranged on a **face-centred cubic space-lattice** (Fig. 10C).

Magnesium, Cadmium, Zinc, Antimony and **Bismuth** crystallize in the **hexagonal-rhombohedral** system.

Tin (in the form usually met with) crystallizes in the **tetragonal** system.

It is significant that most of the *elements* crystallize in the systems (cubic and hexagonal), possessing high degrees of symmetry, although among compounds containing three or more different atoms crystal-systems with low degrees of symmetry (rhombic, monoclinic and triclinic) are more generally met with. It is impossible to go into details of the explanations suggested, but it may be stated generally that it is only to be expected that an ordered assemblage of atoms of a single kind will possess a higher degree of symmetry than an ordered assemblage containing atoms of several different kinds.[1]

Isomorphism.[2] It is not surprising to find that substances having analogous formulæ frequently crystallize in the same form. The following substances, each composed of an alkali-metal joined with a halogen, crystallize in cubes :—

Sodium chloride $NaCl$; Potassium chloride KCl ;
Potassium bromide KBr.

Without doubt, the crystal-architecture is the same in each case.

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[1] One explanation was given by W. Barlow and W. J. Pope, *Trans. Chem. Soc.* **91** (1907), 1150, who assumed the atoms to be incompressible but deformable spheres. The most natural and compact methods of packing balls of equal size in a box lead to arrangements possessing either cubic or hexagonal symmetry. Where the box contains balls of different kinds and sizes, arrangements of lower symmetry are obtained. Sir J. J. Thomson, *Phil. Mag.* **43** (1922), 721, takes into account the valency electrons which are supposed to exist between the metallic atoms in the crystalline state, and is thus able to correlate the crystalline character of the metallic elements with their valency. He shows that the cubic, hexagonal and tetragonal systems are to be expected among elements— a conclusion in complete harmony with the facts. Elements with one valency electron should possess cubic symmetry, whilst divalent elements should possess hexagonal or tetragonal symmetry. It is certainly noteworthy that most of the elements of Groups IA and IB (sodium, lithium, copper, silver and gold) are cubic, whilst most of those of Groups IIA and IIB (magnesium, zinc, cadmium) are hexagonal. However, calcium is believed to be cubic.

[2] The internal structure of mixed crystals, as revealed by the X-ray method, is discussed by L. Vegard and H. Schjelderup, *Phys. Zeitsch.* **18** (1917), 93 ; L. Vegard, *Zeitsch. Phys.* **5** (1921), 17. Compare the views of G. Tammann, *Zeitsch. Metallkunde*, **13** (1921), 406.

Similarly crystals of Magnesium sulphate $MgSO_4.7H_2O$ and Zinc sulphate $ZnSO_4.7H_2O$ are rhombic prisms almost indistinguishable from one another in appearance, although slight differences in the angles between faces can be found if the two crystals are measured accurately. Here also the crystals are evidently built up in the same way; the metal (zinc or magnesium) evidently has the same position in the crystal-structure of both salts.

By crystallization of a solution containing a mixture of zinc and magnesium sulphates it is easy to obtain crystals—perfectly uniform in character—containing both metals; the two metals may be present in any desired proportions. If a series of such **" mixed crystals "** are prepared, ranging from pure zinc sulphate at one end to pure magnesium sulphate at the other, it is found that the angle between the faces varies gradually as the zinc is replaced by magnesium. Evidently the *rôle* of the metallic atoms in the mixed crystals is filled partly by zinc atoms and partly by magnesium atoms. The mixed sulphates can be written $(Zn,Mg)SO_4.7H_2O$. Pairs of salts which have the same form, and which give rise to mixed crystals, are said to be **isomorphous.**

The vague, and therefore convenient, term " solid solution " is often applied in speaking of cases of this kind. In a mixed crystal containing both zinc and magnesium sulphates, we can describe the zinc sulphate as being held in " solid solution " in magnesium sulphate, or the magnesium sulphate as being held in solid solution by the zinc sulphate.

Glasses. If a liquid substance is cooled very quickly to a temperature far below the ordinary freezing-point, the movement of the molecules may become greatly reduced before time has been allowed for the arrangement of atoms into the definite crystal-structure described above. In such a case a glass is formed. A glass, owing to the small thermal movement of the molecules, possesses as great rigidity as a crystalline solid. It is possible that in a glass the molecules may actually be linked up in chains, but, since the arrangement is chaotic, and not ordered as in a crystal, a glass will have the same properties when tested in all directions. It possesses, for instance, no cleavage planes, or directions along which it can break with especial ease. A glass is regarded by some writers as a liquid of such extraordinary high viscosity as to be practically rigid. When heated, glasses gradually soften, becoming more and more like ordinary liquids as the temperature rises; there is no definite melting-point, such as is observed in the case of crystalline solids. If a glass is preserved for some time at a temperature a little below the true melting-point of the crystalline form of the substance, "**devitrification**" usually sets in, and the glass gradually changes to a crystalline mass, the atoms arranging themselves to produce the more stable structure.

Many salts are difficult to obtain as glasses, but silicates, borates and phosphates are readily obtained in the glassy form even when the cooling is fairly slow. Metals also are thought to be converted in part to a vitreous or glassy condition when subjected at low temperatures to violent mechanical treatment, which annihilates the crystal-structure of the material, and leaves the metal in a practically amorphous, structureless condition.

Solutions. A striking effect often noticed when a solid and a liquid are brought into contact is the "dissolution" of the solid by the liquid or "solvent" to form a homogeneous **solution.** Apparently the molecules of the solvent moving past the surface of the solid are able—as a result of their violent thermal movement—to drag away material into the liquid phase; the dissolved material (or "solute") comes thus to share the thermal agitation of the liquid molecules. The process continues until the concentration of the solution reaches the "solubility limit," after which no more solid is dissolved; the solution is then said to be **saturated.** If a **supersaturated** solution, that is a solution having a concentration higher than the "solubility limit," is brought into contact with the solid, the reverse process, "crystallization," commences, and continues until the concentration is reduced to the solubility limit, at which equilibrium is once more established. Evidently the equilibrium between a solid and its saturated solution is reached when the two opposing processes,

(1) *dissolution*, or passage of solid into the liquid phase, and
(2) *crystallization*, or passage of dissolved material on to the solid phase,

take place with equal velocity, and thus balance one another.

In the discussion of a very dilute solution, the term "molecule" recovers the exact meaning which it possesses in the case of gases. For the ultimate particles of the solute must be separated—in a dilute solution—by distances which are large compared to the particles themselves. It should, however, be remembered that they are not separated by space—as in the case of gaseous molecules—but by an atmosphere of solvent. The dissolved molecule is sometimes composed of two or three gaseous molecules "associated" together. But even more common than "**association**" is the opposite phenomenon, "**dissociation.**" For instance, an aqueous solution of sodium chloride does not contain NaCl molecules to any large extent; the charged atoms or "ions," Na˙ and Cl′, appear to move about independently at appreciable distances from one another. This kind of dissociation will be considered further at a later stage.

As a result of thermal movement, dissolved molecules, or ions, frequently collide with one another, and may interact. In fact, most of our chemical reactions are conveniently carried out in solution.

Controversy has raged over the question as to whether the solvent and solute are "chemically united." The fact that the process of solution is often accompanied by heat-evolution, in spite of the fact that it involves passage from the solid to the liquid state, points to some real chemical combination in those cases. Moreover, it is difficult to think that the solvent could drag the solid into solution without some form of union with it. Undoubtedly, in many cases, the forces binding the solute to the solvent are similar to those which exist between the molecules of the solvent itself. This view finds support in the fact that a solvent generally dissolves most readily those solids which have a composition like to itself ("Similia similibus solvuntur"). For instance, the solid hydrocarbons are very soluble in liquid hydrocarbons, but have only an extremely small solubility in water. Salts containing oxygen, on the other hand, are, in general, freely soluble in water, but nearly insoluble in liquid hydrocarbons.

In certain cases—notably in the dissolution of oxides in water—very marked chemical combination accompanies the process with the formation of substances having definite and distinct polar formulæ. Thus sodium oxide (Na_2O) with water forms sodium hydroxide ($NaOH$), whilst nitrogen pentoxide (N_2O_5) forms nitric acid (HNO_3). It is conceivable that in many other cases where solution is accompanied by a rise in temperature the closer type of combination here suggested may also occur, although often we have no means of verifying the suggestion.

The solutions of salts and simple substances—in which the solute molecules are very small—appear to be completely clear and homogeneous. As we pass to solutions in which the dispersed particles of the "solute" are bigger, the appearance becomes visibly turbid; such solutions are known as **colloidal** solutions, and it is often possible—by means of an instrument called the "ultra-microscope"—actually to observe the "colloidal particles" of the solute. It is interesting to note that the particles may be seen in a state of motion ("Brownian Movement"), which may, indeed, be regarded as the thermal agitation. From colloidal solutions we can pass by imperceptible steps to fine suspensions, and thence to coarse suspensions, such as are made by shaking up sand in water. The Brownian Movement rapidly diminishes as the particles become bigger. A suspension of sand in water clearly constitutes a heterogeneous (or two-phase) system, but the difference between a heterogeneous "suspension" and a homogeneous "solution" is only one of degree, the so-called "colloidal solutions" constituting a link between the two.[1] Colloidal solutions are further considered in Chapter VII of this volume.

A word must be added regarding the mutual solubility of two liquids. If the two liquids are alike, they will probably mix in any proportions to form a single phase. If they are quite unlike they will form two separate layers, the lighter liquid resting on the heavier liquid, and being separated from it by a well-marked boundary showing a high interfacial tension—the sign of discontinuity. If the boundary is disturbed by the agitation of the liquid with a stirring-rod, the interfacial tension, aided by the force of gravity, pulls the surface "taut" again as soon as the stirring ceases.

Frequently, however, there is a partial "miscibility," the lighter layer dissolving a little of the heavier liquid, and the heavier liquid dissolving a little of the lighter. An interesting case is that of phenol and water. If these two substances are shaken together at the ordinary temperatures, and allowed to stand, they separate into two liquid layers, the upper one consisting of a solution of phenol in water, whilst the lower one is a solution of water in phenol. However, as the temperature is raised, the water of the upper phase is able to dissolve more phenol, whilst the phenol of the lower phase is able to dissolve more water. The two layers thus become more alike in composition, and the interfacial tension—the sign of discontinuity at the boundary—diminishes. Finally at 68·9° C. the composition of the two phases becomes identical, and the boundary vanishes. Above that temperature the liquids are miscible in all proportions.[2]

Surface Adsorption. It has already been pointed out that the molecules at the boundary of a liquid or at the interface between two liquids are in a special condition, and that the contractile forces known as "surface tension" or "interfacial tension" are the result of this condition. The situation of the atoms at the surface of a solid substance likewise requires special consideration. Since, however, the solid possesses rigidity, the surface cannot shrink and surface phenomena of a rather different character are met with.

Imagine a crystal, such as mica, split into two halves, along a cleavage plane. The forces, which before the splitting united the two halves together, are now available for the attachment of fresh atoms to the newly exposed surface. Accordingly the surface, unless preserved in vacuo, readily becomes covered with a film of "adsorbed" air or moisture, held chemically by the newly available forces. As a result a freshly exposed surface has different properties to an old surface; it possesses, for instance, different frictional properties and a different electrical conductivity.[1]

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[1] See J. Perrin, "Atoms"; translation by D. Ll. Hammick (Constable).

[2] V. Rothmund, *Zeitsch. Phys. Chem.* **26** (1898), 433.

It is probable that the adsorbed film upon a plane surface is not more than one molecule thick.[2] Adsorption is a purely surface phenomenon; porous materials adsorb more freely than do compact materials mainly because they have a far larger surface. The adsorbed layer of air, moisture or grease is often extremely difficult to remove by mechanical means or by heat, being apparently held by forces similar to those responsible for chemical combination. The tendency to adsorption depends on the nature of both the solid and the gas; hydrogen is adsorbed by platinum far more readily than the inert gas argon, for instance.

Interfacial Energy. Interfacial tension exists at the boundary where a liquid comes in contact with a solid and has a most marked influence upon the behaviour of the materials. The behaviour is most easily expressed by the principle of "surface energy." A certain amount of work must be performed in overcoming the forces of interfacial tension if we are to increase the area of the surface of contact between two different materials. Thus we can regard a certain amount of "interfacial energy" involved in the existence of any interface; the interfacial energy per unit area (at any given temperature) depends on the nature of both materials, being in general least when the two materials are similar in character. Now consider a drop of liquid placed on the surface of a solid; it may either remain as a drop, or it may spread itself as a film over the surface of the solid. Such a spreading will increase the area of contact between liquid and solid and between liquid and air, but it will decrease the area of contact between solid and air. If, as a whole, the spreading would involve an *increase* in energy, it can only take place if mechanical work is applied by some outside agency to *force* the liquid over the solid. If, however, the spreading involves a *decrease* in energy, then it will take place spontaneously without any interference from outside; in such a case the liquid is said to "wet" the solid.

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[1] See W. B. Hardy, *J. Soc. Chem. Ind.* **38** (1919), 7; T. W. B. and J. K. Hardy, *Phil. Mag.* **38** (1919), 32. Compare, however, the somewhat different standpoint of H. M. Budgett, *Proc. Roy. Soc.* **86** (1912), 25.

[2] I. Langmuir, *J. Amer. Chem. Soc.* **38** (1916), 2221; **39** (1917), 1848.

If the values of the interfacial energy (per unit area) between the solid (S), liquid (L) and air (A) be expressed by the symbols σ_{SL}, σ_{SA} and σ_{LA}, then the alteration of surface energy due to the drop spreading itself over an area a must be

$$a(\sigma_{SL} + \sigma_{LA} - \sigma_{SA})$$

Only if this is negative will the liquid spread spontaneously over the surface of the solid. In other words, if

$$\sigma_{SA} > \sigma_{SL} + \sigma_{LA}$$

the liquid will "wet" the solid. If this relation does not hold good, the liquid will not "wet" the solid, but will remain gathered in small drops.

If a narrow glass tube is pushed vertically below the surface of water the water will rise in the tube, because such a movement involves a decrease in the energy connected with the interfaces water, glass and air; on the other hand, if a glass tube is pushed into mercury the mercury stands lower in the tube than outside.

Again, if a pasty mixture of white lead and water is churned up with linseed oil, the oil expels the water from the paste, and at the end we are left with a viscous mixture of oil and white lead, along with a separate watery phase (free from white lead) above. The expulsion of the water by the oil takes place because it involves a decrease in the interfacial energy of the system. The phenomenon is of some importance in the manufacture of mixed paints.[1] Likewise, if a fine powder is shaken up with two immiscible liquids, it may enter one or other of the liquids, or alternately it may adhere to the interface between the liquids. Some powders do the one thing and some the other; it is the relative values of the interfacial energy existing between the three materials that settles which will occur. This is a matter which will be referred to again in connection with the flotation of ores.

If a metal is allowed to stand in contact with a corrosive liquid which acts on the metal so as to produce a solid corrosion product, this solid product may either cling tenaciously to the interface between solid and liquid, in which case it is likely to interfere with further corrosion, or it may pass readily into the liquid, and interfere but little with further action. A comparatively slight alteration in the character either of the metal or the liquid may have a striking effect in determining whether the corrosion product shall form a protective film or not.[2]

When a solution comes in contact with a solid, "adsorption" often occurs at the interface, where such adsorption leads to the lowering of the interfacial energy of the system. Thus when the interfacial tension between the solid and solution *decreases* with the concentration of the solution, the solute will tend to collect at the interface, and the concentration of the solution next to the solid is higher than that of the body of the solution. It is well known to analysts how tenaciously certain soluble salts cling to certain precipitates; in many cases it is almost impossible to wash the precipitates effectively owing to the adsorption. Again, a solution of potassium permanganate, when run through a bed of sand, may come through colourless at first, the salt being adsorbed at the surface of the sand.

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[1] Compare W. Reinders, *Chem. Weekblad*, **10** (1913), 708.

[2] Compare U. R. Evans, *Trans. Faraday Society*, **18** (1922), 1.

The opposite effect, known as "negative adsorption" (or preferential adsorption of solvent) is also known. This occurs where the interfacial tension *increases* with the concentration, and consequently the solution becomes more dilute at the area of contact with the solid than elsewhere. Blood charcoal shows positive adsorption towards potassium bromide, and negative adsorption towards sodium chloride; in the case of potassium chloride, there is positive adsorption at high concentrations, and negative adsorption at low concentrations.[1]

The latent forces existing at the free surface of a substance are also manifested in the phenomena of "seizing" and "friction." Two perfectly clean, smooth metallic surfaces, when brought into contact, will often adhere together; but the presence of an adsorbed film on the metal is usually sufficient to prevent this adhesion, because the latent forces—which would otherwise be responsible for the adhesion—are employed in binding the adsorbed substance to the metal. Oily substances are especially efficient in reducing the adhesion between two metals brought into contact; hence the use of lubricants in machinery to reduce friction and eliminate the danger of seizing.

The effect of adhesive forces becomes very marked in the case of very small particles, because very small particles have a large surface area in comparison to their volume. The tendency of ultra-microscopic particles to join together to form aggregates will be met with repeatedly in colloid chemistry.

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[1] Y. Osaka, *Mem. Coll. Sci. Kyōtō*, **1** (1915), 257.

IV. Chemical Reactions and Chemical Equilibria

Acids, Bases and Salts. All the elements, except the inert gases and fluorine, can be made to combine with oxygen, yielding **oxides**. The oxides of non-metals commonly combine with water to give **acids**; thus sulphur trioxide (SO_3) combines with water (H_2O) to yield sulphuric acid (H_2SO_4). A few of the oxides of the metals, for example the higher oxide of chromium (CrO_3), have also an acidic character. In general, however, metallic oxides have basic properties. Many of the metals possess oxides which are nearly insoluble in water, but the oxides of the metals of Group IA combine with water with avidity, yielding soluble hydroxides which are called **alkalis**. Thus sodium oxide (Na_2O) combines with water to give sodium hydroxide (NaOH).

Acids and alkalis are usually distinguished by their action upon certain colouring materials; an acid, for instance, will turn blue litmus red, whilst an alkaline solution will turn red litmus blue; phenol-phthalein is turned pink by alkalis, but the addition of an acid destroys the pink colour.

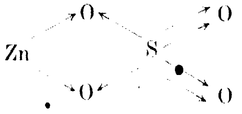
Oxy-salts are the products of combination between basic oxides and acidic oxides. They are often conveniently prepared by neutralizing the solution of an acid with an alkali, or with a basic oxide, water in this case being produced in the reaction; they are also in many cases produced when metals are dissolved in acid, hydrogen gas being evolved. Zinc sulphate ($ZnSO_4$), for example, can be produced in three ways:—

$$ZnO + SO_3 = ZnSO_4$$
$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$$
$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Zinc sulphate, $ZnSO_4$, may be considered as a molecular compound of zinc oxide and sulphur trioxide, and expressed thus:—

$$ZnO.SO_3$$

It is probably more correct to regard it as a compound formed through the transfer of electrons between the atoms as indicated by the following structural formula:—



Too much importance, however, should not be attached to the so-called structural formulæ of inorganic salts, since the very reactivity of these bodies is an indication that the atoms are not linked together in definite positions, like those of carbon compounds, but are probably arranged in different ways at different instants. Structural formulæ will be only rarely suggested in this book.

Zinc oxide is an example of an "**amphoteric**" oxide; whilst normally behaving as a basic oxide, it can also function as an acidic oxide. For instance, it will dissolve in the strong alkali, sodium hydroxide, yielding a salt called sodium zincate, $Na_2O.ZnO$ or Na_2ZnO_2, in which the zinc oxide plays the part of the acidic oxide.

Certain acids exist which contain no oxygen. They are formed simply by the combination of non-metals with hydrogen; aqueous solutions of the compounds hydrogen chloride (HCl), hydrogen iodide (HI) and hydrogen sulphide (H_2S) have acidic properties towards litmus; when the solutions are treated with basic metallic oxides, or hydroxides, the chlorides, iodides or sulphides of the metals are produced:—

$$2HCl + Zn(OH)_2 = ZnCl_2 + 2H_2O$$

The chlorides, iodides and similar compounds are generally grouped, along with the oxy-salts mentioned above, under the general term "**Salt.**" The same compounds may be prepared free from water by direct combination of the metals and non-metals:—

$$Zn + Cl_2 = ZnCl_2$$

Just as two oxides—one more basic than the other—combine to form oxy-salts, so also are stable products formed by the combination of two chlorides, two sulphides or two cyanides, for example:—

$$\begin{aligned} 2KCl + PtCl_4 &= K_2PtCl_6 \\ K_2S + CS_2 &= K_2CS_3 \\ KCN + AgCN &= KAg(CN)_2 \end{aligned}$$

The three reactions above give rise to substances very stable in solution: the products are rather illogically known as "complex salts," although they are probably no more complex than the oxy-salts which are formed by the combination of two oxides. Some compounds of a similar nature, such as carnallite $KCl.MgCl_2.6H_2O$, appear to break up into their components almost completely when dissolved in water, and in such cases the term "double salt" is employed; a solution of carnallite behaves practically as though it contained a mixture of potassium and magnesium chlorides. There is, however, no sharp distinction between "double" and "complex" salts; some compounds of this character split only partially into their components when dissolved.

Dissociation of Salts in Solutions. When a crystalline salt is dissolved in water it is believed to suffer two kinds of dissociation:—

(1) **Hydrolysis**: a splitting into the acid and base from which it is supposed to be derived.

(2) **Electrolytic Dissociation** or **Ionization**: a splitting into electrically charged ions, of which the "positive ion" consists of the most characteristic metal present, bereft of some or all of its valency electrons.

Both types of dissociation are probably incomplete or "balanced" reactions, undissociated salt being in equilibrium with the products of dissociation. Thus:—

$$\mathrm{ZnCl_2 + 2H_2O} \begin{array}{l} \nearrow \mathrm{Zn(OH)_2 + 2HCl} \text{ (Products of Hydrolysis)} \\ \searrow \mathrm{Zn^{\cdot\cdot} + 2Cl' + 2H_2O} \text{ (Products of Ionization)} \end{array}$$

Each kind of dissociation is favoured by an increase in the quantity of water present; hydrolysis is also greatly favoured by a rise of temperature.

That both types of dissociation may be present in the same solution is suggested by the following experiments. If a solution of ferric chloride ($FeCl_3$) is placed in a parchment vessel surrounded by pure water, hydrochloric acid (HCl) diffuses through the parchment, whilst ferric hydroxide ($Fe(OH)_3$) remains in the vessel; in such a case it is the products of hydrolysis which are separated from one another, the process being known as **dialysis**.[1] If, however, two metal electrodes are immersed in the ferric chloride solution, and an electric current is passed between them, metallic iron is formed at one electrode and chlorine at the other; here it is the products of ionisation which are obtained, the process being known as **electrolysis**.

Hydrolysis is most marked in salts in which either the acidic or basic oxide is weak. Sodium carbonate is alkaline to litmus, owing to hydrolysis, carbon dioxide being but a feeble acid. On the other hand, the solutions of many metallic salts have an acid reaction owing to the weakness of the base, and readily deposit insoluble metallic hydroxides or basic salts.

The following table[2] shows the percentage hydrolysis of several metallic salts at 100° C. It will be noticed how much the hydrolysis increases with the dilution :—

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[1] See M. Neidle and J. Barab, *J. Amer. Chem. Soc.* **39** (1917), 71.

[2] The table is prepared from determinations given by C. Kullgren, *Zeitsch. Phys. Chem.* **85** (1913), 466.

Salt.	Concentration.	Hydrolysis. Per cent.
Aluminium chloride ($AlCl_3$) . . .	N/32	9·92
	N/512	47·68
Aluminium sulphate ($Al_2(SO_4)_3$) . .	N/64	9·64
	N/1024	48·22
Mercuric chloride ($HgCl_2$) . . .	N/32	1·35
Cupric chloride ($CuCl_2$) . . .	N/32	0·612
Cupric nitrate ($Cu(NO_3)_2$) . . .	N/32	0·648
Lead nitrate ($Pb(NO_3)_2$) . . .	N/32	0·400
Ammonium nitrate (NH_4NO_3) . .	N/32	0·0776
Ammonium chloride (NH_4Cl) . .	N/32	0·0786
Zinc chloride ($ZnCl_2$)	N/32	0·0760
Zinc nitrate ($Zn(NO_3)_2$) . . .	N/32	0·0470
Cobalt chloride ($CoCl_2$) . . .	N/32	0·0196
Nickel chloride ($NiCl_2$) . . .	N/32	0·0194
Magnesium chloride ($MgCl_2$) . .	N/8	0·00266

Dissociation into charged ions is a more general phenomenon than hydrolysis, and has already been referred to in connection with the electronic theory of combination. In sodium chloride, the elements are believed to be held together by the transfer of an electron from a sodium atom to a chlorine atom, this transfer causing each atom to assume the "inert gas type" :—

$$Na \rightarrow Cl$$

The system produced is so stable that, when the salt is dissolved in water, the two charged atoms (the sodium atom having lost an electron, and the chlorine having gained an electron) are able to move about as though they were distinct molecules. They are called **ions,** and are written :—

$$Na^{\cdot} \text{ and } Cl'$$

the dot and dash representing a positive and negative charge respectively. When an electromotive force is applied to the solution it is believed merely to have a "directive influence" on the thermal movement which is already in existence. The "directive influence" causes the metallic ions to move to the negative electrode (or cathode), whilst the chlorine ions move to the positive electrode (or anode); the former are, therefore, known as cations, and the latter as anions.

It is to be noticed that solutions which are believed—for purely chemical reasons—to be "ionized," conduct electricity, whilst unionized solutions, for instance solutions of sugar, are non-conductors. Pure water, which is ionized in a very minute degree into the ions $H^{\cdot}$ and OH', has a very feeble conductivity.[1]

Some other examples of the ionization of salts and complex salts are given below :—

$$Na_2SO_4 \rightleftharpoons 2Na^{\cdot} + SO_4''$$
$$K_2PtCl_2 \rightleftharpoons 2K^{\cdot} + PtCl_6''$$
$$KAg(CN)_2 \rightleftharpoons K^{\cdot} + Ag(CN)_2'$$

Acids ionize in the following way :—

$$H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4' \rightleftharpoons 2H^{\cdot} + SO_4''$$
$$HCl \rightleftharpoons H^{\cdot} + Cl'$$

It is believed that **Hydrion** ($H^{\cdot}$), the nucleus of the hydrogen atom bereft of its single electron, is the essential component of all acids. Similarly, it is thought that the essential component of all alkalis is the negatively charged group, **hydroxyl** (OH'), which is obtained by ionization thus :—

$$NaOH \rightleftharpoons Na^{\cdot} + OH'$$

Acids which are completely dissociated, yielding plenty of hydrion, are "strong acids," whilst those only partially dissociated are "weak acids." The "strongest" acids, nitric and hydrochloric, are usually stated to be dissociated to an extent of about 93 per cent. in decinormal solution. Carbonic acid, a weak acid, is only dissociated to the extent of about 0·174 per cent., and many organic acids are still less dissociated. Other numbers of this sort are given in a table in Chapter V (page 245), and their interpretation is discussed in Chapter VI.

Similarly, the hydroxides of metals which are fully ionized are strongly alkaline, whilst those which are partially ionized have only feeble alkaline properties. It should be noted that the metals of Groups IA and IIA are almost alone in yielding strongly alkaline hydroxides. As we pass to other groups the alkaline and basic character of the metals tends to disappear, and with it the solubility of the oxides.

The neutralization of an acid by an alkali is commonly written in the form :—

$$NaOH + HCl = NaCl + H_2O$$

If, however, the acid, alkali and salt are regarded as completely ionized, the reaction can be expressed in ionic language thus :—

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' \quad Na^{\cdot} + Cl' + H_2O$$

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[1] The arguments in favour of the dissociation theory of electrolytic dissociation are well summarised by the originator of the theory, S. Arrhenius, *Trans. Faraday Soc.* **15** (1919–20), 10; and the general position is ably discussed by G. Senter, *Trans. Faraday Soc.* **15** (1919–20), 3.

Omitting the terms common to both sides of the equation, we obtain :—

$$OH' + H^{\cdot} = H_2O$$

The neutralization of *any* strong acid by *any* strong alkali can thus be expressed by this one equation. In other words, the neutralization of all strong acids and alkalis is essentially the same process, and it is not surprising to find that, if equivalent quantities are considered, the heat evolved is the same in all cases. This is not true if we consider weak, partially ionized acids and alkalis, amongst which considerable variations in the "heat of neutralization" are met with.

Hydrolysis, the change diametrically opposite to that of salt-formation, has itself received a rather special explanation from the supporters of the ionization theory. Water is, to a very minute extent, split up into ions, thus :—

$$H_2O = H^{\cdot} + OH'$$

although such a small proportion of the molecules are affected in this way that the hydrogen ion concentration of pure water is only about 10^{-7} normal. When a little salt is introduced into pure water it dissociates fairly completely into its ions, thus :—

$$\begin{aligned} NaCl &= Na^{\cdot} + Cl' \\ FeCl_3 &= Fe^{\cdot\cdot\cdot} + 3Cl' \\ \text{or } KCN &= K^{\cdot} + CN' \end{aligned}$$

If, as in the case of sodium chloride, the acid concerned is a strong acid and the base a strong base, no further change occurs. If, however, as in ferric chloride, the base corresponding to the salt is a weak one, its ionization being nearly as low, or lower, than that of water, the following reaction occurs with the small amount of hydroxyl present in the water :—

$$Fe^{\cdot\cdot\cdot} + 3\,OH' = Fe(OH)_3$$

Since the corresponding quantity of hydrion is left free the solution acquires an acid reaction. Similarly, if the acid of the salt is a weak one, as in the case of potassium cyanide, the following change occurs :—

$$CN' + H^{\cdot} = HCN$$

and the solution is left alkaline.

Most of the precipitation processes, which are of such importance in inorganic analysis, can be represented as reactions between ions. If by the combination of two ions a salt can be produced which has a limited solubility in water, precipitation is to be expected when solutions containing these ions are mixed. Silver chloride

(AgCl), for example, is very sparingly soluble in water. If a solution of an ionizing chloride is treated with a solution of an ionizing silver salt, such as silver nitrate ($AgNO_3$), precipitation of solid silver chloride will occur. Thus silver nitrate is said to be a "reagent" for the detection of ionizing chlorides.

Oxidizing and Reducing Agents. Where a metal has a variable valency, forming more than one series of compounds, the compounds corresponding to the higher valency can often be made to furnish oxygen—or its equivalent—to other substances, and are then known as **oxidizing agents.** Likewise the compounds corresponding to a lower valency often absorb oxygen—or its equivalent—and then function as **reducing agents.** Thus manganese dioxide (MnO_2) is an oxidizing agent, whilst manganous oxide (MnO) is a reducing agent. In general, when an oxidizing agent is mixed with a reducing agent, they will react, the first becoming reduced and the second becoming oxidized. Thus potassium permanganate, a strong oxidizer containing heptavalent manganese, reacts in acid solution with ferrous sulphate, a reducer containing divalent iron; the manganese is reduced to the divalent condition, whilst the iron is oxidized to the trivalent (ferric) state. The reaction is generally written:—

$$10FeSO_4 + 2KMnO_4 + 9H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 2KHSO_4 + 8H_2O.$$

The working out of such a complicated equation may at first seem difficult, but it becomes simple if it be assumed that the reaction occurs between heptavalent manganese (Mn^{VII}) and divalent iron (Fe^{II}), with divalent manganese (Mn^{II}), and trivalent iron (Fe^{III}), as final products. It is clear that, if the total electric charges are to remain constant, the metals must act in the proportions shown by the equation:

$$Mn^{VII} + 5Fe^{II} = Mn^{II} + 5Fe^{III}.$$

And this at once indicates that the proportion in which the permanganate and ferrous sulphate molecules enter into the reaction is

$$KMnO_4 : FeSO_4 = 1 : 5.$$

The above method of calculation is not invalidated by the fact that—as a matter of fact—Mn^{VII} ions have probably no independent existence in the permanganate solution.

The term oxidizer and reducer are often applied in changes which involve no actual transfer of oxygen, but in which some equivalent substance (e.g. chlorine) is transferred. Thus, in the interaction of ferric chloride $FeCl_3$ and stannous chloride $SnCl_2$, according to the equation

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4;$$

the ferric salt is said to be the oxidizing agent, and the stannous chloride the reducing agent.

Homogeneous and Heterogeneous Reactions.—When two substances react together in solution, or in a uniform gas-mixture, the reaction is said to be **homogeneous**; it takes place equally throughout the volume of the solution or gas mixture. The interaction of an acid and alkali in aqueous solution to form a soluble salt is a good example of a homogeneous reaction. On the other hand, the attack of an acid upon a solid piece of metal is an instance of a **heterogeneous** (or two-phase) reaction; here the action is confined to the surface dividing the metal from the acid.

Velocity of a Homogeneous Reaction.[1] Most reactions between inorganic substances occur with great rapidity, the speed being very much greater at high temperatures than low, partly owing to the increased movement of the molecules and partly owing to other causes. The velocity also depends greatly on the concentration of the reacting substances in the solution or mixture; in practically every case the change starts quickly, but as the reaction approaches completion, and the reacting substances become nearly used up, it slows down considerably.

Consider the reaction between tri-ethylamine, $N(C_2H_5)_3$, and ethyl iodide $(C_2H_5)I$:—

$$N(C_2H_5)_3 + (C_2H_5)I = N(C_2H_5)_4I.$$

The change depends upon the atoms of tri-ethylamine and those of ethyl iodide colliding with each other during their thermal movement. If we multiply the concentration of tri-ethylamine n-fold we increase the number of collisions per second n times; if, in addition, we increase the concentration of ethyl iodide n times we again multiply the number of collisions by n. Thus, as the result of increasing the concentration of each reagent n-fold, the rate of interaction is increased n^2 times. Had the collision of three, instead of two, molecules been involved in the change, the same increase of concentration would have increased the velocity n^3 times. Whilst, if only one molecule were concerned in the change, the reactional velocity would be proportional to n.

It has indeed been proved experimentally that the velocity of "bimolecular" reactions such as

$$N(C_2H_5)_3 + (C_2H_5)I = N(C_2H_5)_4I$$

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[1] This subject is discussed in detail by J. W. Mellor in his "Chemical Statics and Dynamics" (Longmans, Green & Co.).

varies as the square of the concentration; whereas that of "trimolecular" reactions such as

$$H\text{-}COONa + 2CH_3\text{-}COO\,Ag = 2Ag + CO_2 + CH_3COOH + CH_3COONa$$

varies as the cube of the concentration. These relations may be regarded as two examples of the **Law of Mass Action**, which states that "the velocity of reaction is proportional to the *active mass* of *each* of the reacting substances."

Reversible Reactions. Homogeneous Equilibrium. The majority of reactions can take place in either direction, according to circumstances; equilibrium occurs when the velocity of the two opposing changes becomes equal. Good examples of "balanced reactions" are to be found in the hydrolysis of salts. If, for instance, ferric chloride is dissolved in water, partial hydrolysis occurs, the solution being found to have an acid reaction:—

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl.$$

On the other hand, if hydrochloric acid is added to ferric hydroxide, a certain amount of salt is always formed:—

$$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O.$$

Whichever end of the scale we start from the same amounts of the four substances should be present when the state of equilibrium

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

is arrived at. If, however, we add excess of one of the four reacting bodies, the equilibrium is disturbed. For instance, if we dilute the mixture by the addition of water, it is clear, by the law of mass-action, that the velocity of the hydrolysis reaction will be increased. The velocity of the opposing reaction of salt-formation will, on the other hand, be reduced by the dilution, and the equilibrium is therefore shifted in such a way as to favour hydrolysis; the increase of hydrolysis which, as already stated, accompanies dilution is therefore explained.

If, however, we add excess of hydrochloric acid to the solution, the reverse action is aided, and the equilibrium is shifted in such a way as to reduce hydrolysis. This is a most important fact in practice. Many metallic salts are hydrolysed by water so readily that they yield—in pure water—a solution which is always cloudy with insoluble hydroxide or basic salt. The cloudiness would be highly inconvenient to the chemist, were it not for the fact that it is generally possible to obtain a clear solution by the addition of a little acid.

Velocity of a Heterogeneous Reaction. The reaction between two phases, or bodies having a different character and separated from one another by a sharp boundary, necessarily depends on the area of that boundary. If a rapid action is aimed at, it is advisable to make the surface of contact as large as possible. Finely divided metals, for instance, are far more quickly attacked by acids or by atmospheric oxygen than the ordinary compact form—a fact mainly due to the large surface area of the finer variety. Again, if it is desired to cause a reaction between a refractory mineral, like corundum, and a fused salt—such as potassium hydrogen sulphate—it is essential to grind the mineral to the very finest powder before heating it with the salt.

Heterogeneous Equilibrium. The Phase Rule.[1] Whilst an increase of surface area between phases has an astonishing effect upon the velocity of a heterogeneous reaction, it can clearly have no effect upon the conditions of final equilibrium between two phases; for the increase will be equally favourable to both the opposing changes, which, in a state of equilibrium, balance one another. Suppose, for instance, a lump of ice is floating in water at 0° C., being in equilibrium with it. If we grind up the ice to powder, we may, by increasing the area, facilitate the passage of material from the solid phase to the liquid, but to the same extent we facilitate the passage of material in the opposite direction. The equilibrium, therefore, is not disturbed, unless, indeed, the powder is made so fine that the effect of interfacial energy has to be taken into account.

A most important generalization, known as the **Phase Rule,** gives valuable information regarding the way in which equilibrium varies with external conditions. In any system of phases in equilibrium it is necessary to know the amount of a certain number of substances present in order to have complete information regarding the composition of each phase; these substances are called "**components.**" Pure water has one component; solid sodium chloride has one component; but a solution of sodium chloride has two components, since, unless we know separately the amount of the water and of the sodium chloride present, our information regarding the character of the solution is incomplete. If P be the number of phases in equilibrium and C be the total number of components, then the "Phase Rule" states that the "Degree of Freedom" (F) of the system is given by the equation:—

$$F = C - P + 2.$$

The Degree of Freedom is "the number of variable factors

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[1] Reference should be made to A. Findlay's book on "The Phase Rule" (Longmans, Green & Co.).

(temperature, pressure and concentration of components) which must be arbitrarily fixed in order that the condition of the system may be completely defined." The meaning of this will become apparent when a few examples have been considered. Fig. 11 is a diagram designed to show the conditions of equilibrium between ice, liquid water and water vapour. Suppose that we wish to know under what conditions all these three forms of water can co-exist? The system would then contain one component and three phases. Thus $C = 1$, $P = 3$; the degree of freedom (F) is

$$F = C - P + 2 = 1 - 3 + 2 = 0.$$

There is, therefore, *no* degree of freedom. That means that it is not necessary to know anything further about the system in order completely to define it. A glance at the diagram shows that this is the case. There is only one point, P, at which ice, water and vapour can co-exist. It corresponds to a temperature of 0·0076° C., and a pressure of 4·6 mm. of mercury; no alternative values are possible. The mere fact that the three phases are present together tells us that the temperature and pressure must have those values; our information about the system is at once complete.

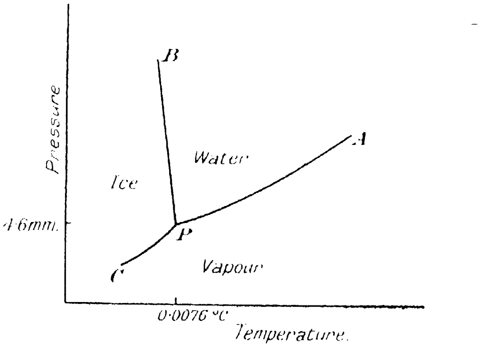

FIG. 11. Equilibrium between Ice, Water and Vapour.

The equilibrium between water and water-vapour allows a degree of freedom equal to

$$F = 1 - 2 + 2 = 1.$$

On the diagram the equilibrium is expressed by the line PA; for every temperature there is a definite pressure (the "vapour pressure"), at which water vapour will be in equilibrium with liquid water. Therefore, if we observe the temperature of the water with a thermometer, the pressure of the vapour in equilibrium with it can be foretold without further measurement. It may be remarked here that if the water is heated to 100° C., the vapour pressure becomes equal to that of the atmosphere. The vapour produced is able at that temperature to force its way out of the vessel in which it is contained, and the liquid is able to "boil."

Finally we may consider the case when there is only the vapour phase present (it is customary to speak of it as "steam," when the liquid and solid forms of water are absent). Since P is now equal to one, we have :—

$$F = 1 - 1 + 2 = 2.$$

There are now two degrees of freedom, and it is possible to vary the pressure and temperature of dry steam separately.

It is desirable next to consider a system with two components. Calcium carbonate gives off carbon dioxide, when heated, calcium oxide being left. The equilibrium is expressed :—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

Here we have two solid phases and one gaseous phase, making a total of three ; the degree of freedom is, therefore,

$$2 - 3 + 2 = 1.$$

Consequently, there is for every temperature one definite pressure of carbon dioxide (the "decomposition pressure") which will be in equilibrium with the two solids. The pressure rises with the temperature, becoming equal to that of the atmosphere at 812°.[1] It is not possible, therefore, to obtain a steady decomposition of calcium carbonate by simple heating under ordinary conditions unless that temperature is exceeded.

The conditions of equilibrium between salts and their solutions may shortly be considered. Unfortunately, a model is needed to show the effects of varying temperatures, pressure and composition simultaneously. A paper diagram, with only two axes, can show merely the relations between compositions and temperature, or between composition and pressure.

Fig. 12 represents the equilibrium diagram of the system ferric chloride-water.[2] The melting-point of ice is 0° C. ; that is to say, ice is in equilibrium with pure water at 0° C., as is shown by the point A. But the melting-point of ice is lowered by the presence of ferric chloride in water ; this is indicated by the curve AB, which shows the temperatures at which ice is in equilibrium with water containing gradually increasing quantities of ferric chloride.

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[1] H. Le Chatelier, *Comptes Rend.* **102** (1886), 1243.

[2] H. W. B. Roozeboom, *Zeitsch. Phys. Chem.* **10** (1892), 477.

Ferric chloride forms, by combination with water, four definite hydrates :—

$2FeCl_3.12H_2O$	with melting-point	37°
$2FeCl_3.7H_2O$	,, ,,	32·5°
$2FeCl_3.5H_2O$	,, ,,	56°
$2FeCl_3.4H_2O$	,, ,,	73·5°

The melting-points of the pure hydrates—that is, the points at which each hydrate stands in equilibrium with liquid having the same composition—are indicated by the four points—C, D, E and F. But in every case the melting-point is lowered if the liquid contains either more water or more ferric chloride than the solid phase. As a result the true melting-points of the hydrates stand at the maxima of the four curves shown in the diagram.

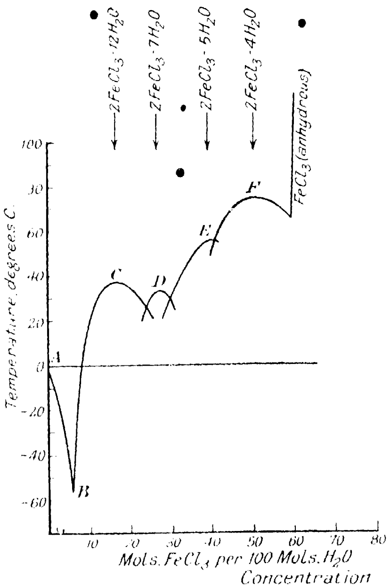

FIG. 12.—Equilibrium Diagram of the System Ferric Chloride-Water.

These curves may be called "the solubility curves" of the various hydrates of ferric chloride. At temperatures above those indicated by the curves the solution is necessarily entirely liquid. When, however, the liquid is cooled down to a temperature below the solubility curve of one of the hydrates, it becomes "metastable" towards that hydrate. If, then, the metastable solution is "inoculated" with a minute crystal of that hydrate, which will provide a nucleus for crystallization, solid will separate from the liquid until conditions of true equilibrium are obtained. Sometimes crystallization may start spontaneously without the provision of a nucleus from outside.

Molecular Weight Measurement. It has just been remarked that the melting-point of ice is lowered by the presence of ferric chloride in the water, and that the melting-point of any one of the hydrates is lowered by the presence of water or ferric chloride in excess of the proper quantity in the liquid phase. This is a perfectly general phenomenon, and is very readily understood. At 0° C. ice and pure water can co-exist without either phase increasing at the expense of the other; this merely means that as many molecules leave the water for the ice as enter the water from the ice. If, however, the pure water is replaced by water "contaminated" with ferric chloride, there will be a lower rate of movement of molecules across the boundary in the direction "water ⟶ ice," simply because the liquid is no longer pure water, but water diluted or rarefied by the presence of ferric chloride. On the other hand, the opposite movement across the boundary in the direction "ice ⟶ water" is in no way reduced, because the solid phase has not received the contamination. Therefore equilibrium is upset, and can only be restored if the temperature is lowered—a change which is naturally favourable to the maintenance of the solid state.

It is universally accepted that the "**depression of the freezing-point**" is—for very dilute solutions—proportional simply to the number of molecules of the dissolved substance in unit volume of the solution, and is independent of the nature of the "solute" or dissolved substance. Consequently the measurement of the depression can be used as a means of obtaining information regarding the state of molecular aggregation of the solute. In this way it has been found that solutions of sodium chloride show twice the expected depression of the freezing-point, and contain about twice as many molecules as would be calculated from the formula NaCl. This is explained by the theory of electrolytic dissociation, according to which the molecule of sodium chloride is broken up in solution into two virtually distinct ions, $Na^{\cdot}$ and Cl'. If this explanation is correct, a salt-like calcium chloride, $CaCl_2$, which should produce three ions by ionization, may be expected to give three times the normal depression. Measurements have shown this to be the case, and the result is one of those upon which supporters of the dissociation theory base their arguments.

In addition to depressing the freezing-point, the presence of a dissolved non-volatile substance also diminishes the vapour pressure of the pure solvent. And since the boiling-point is the temperature at which the vapour pressure becomes equal to a pressure of one atmosphere, the effect is equivalent to the raising of the boiling-point. Measurements of the **elevation of the boiling-point** have—like those of the depression of the freezing-point—been used for the determination of molecular weights. In other cases—notably for determining the molecular weight of soap solutions—the vapour pressure of a solution can best be obtained by the observation of the **dew-point.**

Osmotic Pressure. One more phenomenon of dilute solutions must be mentioned at this point. Supposing a porous vessel within the walls of which a membrane of copper ferrocyanide is supported, and the mouth of which is connected to a long vertical tube, is filled with a dilute aqueous solution of sugar, and surrounded by pure water, as is shown in Fig. 13. If the copper ferrocyanide were not present, the thermal movement of the molecules would finally cause the composition of the liquid on both sides of the porous walls to become the same: partly by diffusion of sugar outwards, partly by diffusion of water inwards. But the copper ferrocyanide constitutes a so-called **semi-permeable** membrane; it allows water to pass through it, but not sugar.[1] Consequently the diffusion can take place in one direction only, namely inwards. As a result, the liquid rises in the vertical tube, until the hydrostatic pressure produced by the "head" of the solution is sufficient to stop further flow. The equilibrium value of the pressure is then said to represent the "**Osmotic Pressure**" of the sugar in the solution. The Osmotic Pressure is proportional to the concentration of molecules in the solution, and consequently this sort of experiment can be used for the determination of the molecular weight of a dissolved substance. Since, however, the preparation of suitable ferrocyanide membranes is a matter of difficulty, it is more convenient to employ the "freezing-point" or "boiling-point" methods for this purpose.

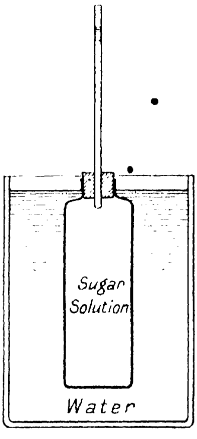

FIG. 13.—Apparatus for demonstrating Osmotic Pressure.

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[1] The action of the semi-permeable medium is discussed by F. Tinker, *Trans. Faraday Soc.* **13** (1917), 133.

When a semi-permeable medium is used to demonstrate the osmotic pressure due to a dissolved substance, it will be observed that the presence of the dissolved substance actually causes a suction of pure solvent into the solution rather than an outward pressure; it has indeed been proposed to call the phenomenon "osmotic suction" instead of "osmotic pressure." It should, however, be noticed that the direction of flow is merely determined by the conditions of the experiment. The membrane is impermeable to sugar, and since there is pure water outside the vessel, and water diluted with sugar inside it, there is a resultant flow of water inwards so as to reduce the difference in concentration. If, however, the membrane were permeable to sugar and not to water, the flow would take place in the opposite direction.[1]

The osmotic pressure can be regarded as the pressure that causes diffusion—the pressure which compels the solute to distribute itself uniformly through the volume of the solvent, just as a gas distributes itself throughout the whole volume of a vessel into which it is introduced. And, just as the gaseous pressure is due to the kinetic movement of the molecules composing the gas, so the osmotic pressure is merely a sign of the motion of the molecules in the solution, and bears the same sort of relation to the temperature and to the volume of the solution containing a gram-molecule of solute as does the pressure of a gas. In fact, for very dilute solutions, the law connecting the osmotic pressure, the dilution and the temperature, is analogous to that connecting pressure, volume and temperature in a gas. Thus:—

$$\pi V = RT$$

where π is the Osmotic Pressure
V the volume containing one gram-molecule of solute
T the temperature on the absolute scale
and R the gas constant, the same constant as occurs in the analogous equation

$$PV = RT$$

which determines the pressure and volume of a gas.

Catalysis.[2] The velocity of a chemical change depends very considerably upon the medium in which it is taking place. For instance, if the reaction of the same substances is studied in aqueous solution and again in alcoholic solution, it is found that the velocity is nearly always greatest in aqueous solution. Probably the action of the solvent is only one case of the very general phenomenon known as "catalysis," the action of an apparently inert material in accelerating the interaction of two other substances. The third (apparently inert) substance is called a **catalyst**; occasionally a change appears to be incapable of taking place—at any rate, at low temperatures—in the absence of such a substance. The catalyst is not used up in the reaction, in which, at first sight, it appears to take no part. Since, however, the physical appearance of the catalyst often alters during the reaction, it is probable that the catalyst does take a real part in the change, but is continuously regenerated. In fact, one general interpretation of the action of a catalyst can be given at once. Supposing the direct combination of two substances A and B according to the equation

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[1] Some interesting remarks on Osmotic Pressure are made by J. J. Van Laar, *Proc. Amst. Acad.* **18** (1916), 184.

[2] The subject is fully discussed by E. K. Rideal and H. S. Taylor in "Catalysis: in Theory and Practice" (Macmillan). A good discussion of different theories is given by W. D. Bancroft, *Trans. Amer. Electrochem. Soc.* **37** (1920), 21. See also E. K. Rideal, *Trans. Amer. Electrochem. Soc.* **36** (1919), 195. The theories of W. C. McC. Lewis will be referred to in the section dealing with radiation.

$$A + B = AB$$

does not take place at a given temperature, or takes place only slowly, the presence of a catalyst X may allow the combination to take place readily in two stages:—

$$A + X = AX$$
$$AX + B = AB + X$$

Since X is regenerated at the end of the reaction, a small quantity of catalyst will promote the combination of a very large quantity of the substance. Such a general explanation will, however, scarcely satisfy an inquiring mind, for it may well be asked why the indirect reaction should take place more easily than the direct. The answer to this question is probably different in different cases.

Examples of catalysis are numerous, and may be divided into two main classes, homogeneous and heterogeneous. **Heterogeneous catalysis,** being the more important phenomenon, may conveniently be considered first.

The combination of sulphur dioxide and oxygen to form sulphur trioxide takes place only very slowly at 300°–400° under ordinary circumstances. If, however, the gases are passed over a "contact material," such as spongy platinum, combination takes place readily at that temperature. The change has the character of a surface action, and it is highly desirable to make the surface area of the platinum as large as possible. It is customary, therefore, to precipitate the platinum catalyst within a highly porous mass such as anhydrous magnesium sulphate; a very large active surface is thus obtained, and a high velocity of reaction is attained to.

There is little doubt that the two gases, sulphur dioxide and oxygen, are adsorbed at the surface of the platinum, the atoms being thus brought into closer contact than is possible in the gaseous state. They then react to produce sulphur trioxide, which is at once liberated. It is important, however, that other substances which might be adsorbed at the platinum surface instead of the reagents should be absent. If the sulphur dioxide contains a trace of arsenic—a substance which is readily adsorbed by platinum and tenaciously held by it—the whole adsorptive power of the platinum comes gradually to be taken up by the layer of firmly attached arsenic, and the catalytic activity consequently declines. The catalyst is then said to be "**poisoned**" by the arsenic.[1] Various other substances are known to cause the poisoning of a platinum contact material: cyanogen and carbon monoxide are two more examples. Since many of the substances which are poisonous to the platinum catalyst interfere with the work of the enzymes—the catalysts of living organisms—they have frequently a poisonous reaction upon the human system also. Possibly their effect on the enzymes is similar in character to their effect on platinum; if so, the word "poisoning"—which serves to describe the result of contamination of the platinum catalyst—has been aptly chosen.

Many other examples of chemical changes promoted by a contact material could be given. The gases, oxygen and hydrogen, normally react only at high temperatures; if passed over spongy platinum, they combine readily at low temperatures. Similarly platinum promotes the interaction of ammonia (NH_3) and oxygen to form nitric acid (HNO_3), whilst a nickel catalyst is used to bring about the "hardening" of fats by combination with hydrogen. It should be pointed out that whilst the presence of a contact substance vastly accelerates the velocity of a reaction, it cannot alter the conditions for equilibrium. If it did, we could make an action go backwards and forwards by alternately removing and replacing the contact material, and so obtain perpetual motion. Presumably, therefore, in a reversible reaction, a contact material must accelerate both opposing changes in an equal degree.

In homogeneous catalysis, the catalyst is distributed uniformly throughout the phase in which a reaction is occurring. A great many metals—such as vanadium, manganese and cobalt—which form more than one series of salts are very active as "oxygen-carriers." The reaction of potassium permanganate with oxalic acid in the presence of sulphuric acid according to the equation

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[1] This view of the action of a poison is well discussed by I. Langmuir, *J. Amer. Chem. Soc.* **38** (1916), 2272–2278. See also W. D. Bancroft, *Trans. Amer. Electrochem. Soc.* **37** (1920), 21.

$$2KMnO_4 + 4H_2SO_4 + 5H_2C_2O_4 = 2MnSO_4 + 10CO_2 + 8H_2O + 2KHSO_4$$

normally takes place only when the solution is warmed; but if some manganous salt be added to the solution the reaction starts at ordinary temperatures. The action of a trace of a copper or vanadium salt in promoting the oxidation of an aniline salt to "aniline black" by potassium dichromate, and the action of a salt of cobalt, lead or manganese in causing linseed oil to take up oxygen from the air during the process of "drying," may here be mentioned. In all these cases it appears that the catalyst first takes up oxygen from the true oxidizing agent, forming a higher oxide or a salt of a higher oxide, which then passes on the oxygen to the substance requiring oxidation; the original catalyst is thus regenerated, and the process is repeated until oxidation is complete.

V. ANALYTICAL CHEMISTRY AND THE DETERMINATION OF ATOMIC WEIGHTS

The practical details which must be followed in carrying out the various analytical operations are described in the numerous excellent handbooks dealing with the subject; in this section it is only necessary to make some general remarks upon the principles employed in chemical analysis.

Qualitative Analysis. The methods used for the detection of the individual metals in a compound or a mixture of compounds are very varied. If the compound can be brought into solution by the action of water or an acid, the addition of certain chosen reagents gives information regarding the presence or absence of certain metals. Thus, if silver be present in a solution, the addition of hydrochloric acid will cause the appearance of a white curdling precipitate of silver chloride, soluble in ammonia; if ferric iron be present, the addition of potassium thiocyanate will produce a blood-red coloration, due to ferric thiocyanate. But such tests must not be regarded as infallible; certain complex cyanides containing silver and ferric iron respectively fail to respond to the tests for either metal; if cyanides are present, it is best to decompose them by heating the substance with concentrated sulphuric acid, before performing the test.

Other tests are carried out with a dry substance at a high temperature. Many metals confer a distinctive coloration if added in small quantities to a molten glass. In practice the easily fusible glass obtained by heating borax is employed. Cobalt, for instance, confers a deep blue tint upon a bead of molten borax. Many metals with volatile chlorides can be detected by moistening the substance under examination with hydrochloric acid, and introducing it into a colourless flame; most of the metals of Groups IA and IIA confer a characteristic colour upon the flame; thus sodium produces a yellow colour, potassium a violet colour, and barium a green colour. Where the colour of the flame, as viewed by the naked eye, gives insufficient or uncertain information, it may be examined through a spectroscope; the various spectral lines characteristic of the different metals can be sought for, and the presence or absence of the metals in question established.

Another class of test depends upon the reduction of the metal to the elementary condition. The substance under examination is mixed with sodium carbonate (or a mixture of sodium carbonate and potassium cyanide) and is heated on charcoal in the reducing flame of the blowpipe. If a metallic bead is obtained, the physical character of the bead (which may be malleable or brittle), and in some cases the colour, help to indicate the metal present. Moreover, the more oxidizable metals yield—in addition to a metallic bead—an incrustation of oxide; cadmium gives a brown incrustation, bismuth an orange incrustation, lead a yellow incrustation, antimony a white incrustation, and so on.

Gravimetric Analysis. In order to determine accurately the proportion of a metal present in the material under examination, it is necessary to weigh out a sample, and to convert the whole of the metal present in that sample either

(*a*) to the metallic state,

or (*b*) to the condition of some sparingly soluble compound of constant well-known composition, which can be filtered off and weighed.

The first method is in principle the more simple; the reduction to the metallic state may be carried out in a furnace at a high temperature ("dry assay"), or by the electrolysis of an aqueous solution ("electro-analysis"). For the less easily reducible metals, however, it is better to precipitate the metal from an aqueous solution as some sparingly soluble compound, which can be filtered off from the solution, washed, dried (usually ignited) and weighed. From the weight of the precipitate the weight of the metal present in it is easily calculated.

The choice of a compound suitable for the complete precipitation of a metal is limited by the following requirements:—

(1) The precipitate must be as "**insoluble**" as possible, in order that precipitation may be complete. Often a precipitate which is appreciably soluble in pure water is much less soluble in water containing excess of the precipitant. In some cases (e.g. lead sulphate or potassium platinichloride) alcohol is added to the liquid in which precipitation is to take place in order to reduce the solubility of the precipitate. In many instances, the precipitate should not be washed with pure water, but with water containing a small quantity of a chosen reagent; thus precipitated magnesium ammonium phosphate is usually washed with water containing ammonia, whilst a precipitate of copper sulphide should be washed with water containing hydrogen sulphide.

(2) The precipitate must be thrown down **in a form which can readily be filtered and washed.** The most desirable kind of precipitate is a sandy type consisting of comparatively large grains which do not obstruct the flow of the liquid through the filtering medium. Gelatinous precipitates, consisting of very small par-

ticles clinging together as flocks, give much more trouble; they tend to clog the filter-paper, causing slow filtration, and owing to their voluminous character, and their capacity for the "adsorption" of salts, they are very difficult to wash. Under certain circumstances, substances of this character—although not soluble in the ordinary sense—may enter into "colloidal solution" as minute colloid particles which can pass through the filter-paper. In order to avoid this trouble, and to obtain each precipitate in a form as far as possible adapted for filtration, the conditions prescribed in the practical analytical textbooks must be followed with care; originally these conditions have been arrived at as a result of experience, but recent work in physical chemistry enables us now to assign a reason for many of the precautions in methods which until recently were of an empirical character.

(3) The precipitate when heated under certain specified conditions must yield a **body of constant and well-known composition,** which can be weighed. Often the body produced on heating is essentially different in composition from the original precipitate; thus magnesium is usually precipitated as magnesium ammonium phosphate $MgNH_4PO_4$, but on ignition the precipitate loses ammonia and water and becomes converted to magnesium pyrophosphate $Mg_2P_2O_7$, in which form magnesium is weighed.

Where the precipitate has been filtered through an ordinary filter-paper, it is usually advisable (although not necessary in all cases) to separate it from the filter-paper before ignition. It is, however, impossible to avoid leaving a small amount of precipitate sticking to the filter-paper, and it is customary to burn the filter-paper after the separation and to weigh the ash along with the ignited precipitate. Many compounds, however, suffer reduction during the burning of the filter-paper. Thus silver chloride is decomposed yielding metallic silver, but in this case it is easy to reconvert the silver to the state of chloride by the action of a few drops of nitric and hydrochloric acids, excess of acids being afterwards driven off by heat. Where, however, the precipitate contains a volatile metal, like mercury or zinc, this metal is liable to pass off in the vaporous state when the filter is burnt. In such cases it is best if possible to avoid the burning of the filter-paper. The precipitate may, for instance, be filtered through a piece of filter-paper which has been dried at 110° C. and weighed before use, or alternatively through a perforated Gooch crucible lined with asbestos fibre. In either case, after the precipitate has been brought on to the filter, and washed, the whole is again dried at about 110° C., and weighed.

Volumetric Analysis. Somewhat more rapid, although less accurate, methods of quantitative analysis depend on the process known as "**titration.**" The solution containing the substance to be estimated is placed in a beaker, and a solution of known concentration containing a reagent which will interact with the salt in the beaker is added carefully from a graduated vessel known as a burette, until the analyst judges that sufficient has been added exactly to interact with the liquid in the beaker; this is said to be the "end-point." By reading the burette, it is possible to see at once the volume of the standard reagent, which has been required to react with the solution in the beaker: from this volume, the quantity of metal in the beaker is easy to calculate.

The "end-point" may be recognized by the analyst in one of the following ways:—

(1) A colour change due to one of the reagents may occur when the end-point is reached. Thus when potassium permanganate is added from a burette to ferrous sulphate contained in the beaker, a pink colour appears in the beaker as soon as the permanganate is present "in excess" of the quantity needed to react with the ferrous salt.

(2) Where the reaction itself produces no colour change, an "*indicator*" may be added before titration. In the titration of an acid by an alkali, a drop of phenol-phthalein is added to the acid liquid; as soon as the alkali is in excess, a pink colour appears.

(3) Where the presence of the indicator in the beaker would interfere with the reaction, the method of a "*side-indicator*," may be used. In the titration of ferrous chloride with potassium dichromate, the progress of the reaction is checked by removing drops of the liquid and testing them with drops of potassium ferricyanide on a porcelain slab. As long as ferrous iron remains in the beaker, a blue precipitate is produced where the solution and the ferricyanide come into contact; after the end-point has been reached, no precipitate is obtained. This method is obviously slow.

(4) An *electrometric* method of determining the end-point may be used. Such methods are discussed on pages 332–335.

Although any solution of accurately known concentration can be employed in the burette in volumetric analysis, the calculations are greatly simplified if the standard solution employed is either

normal (N) containing one gram-equivalent weight per litre

decinormal $\left(\frac{N}{10}\right)$,, $\frac{1}{10}$,, ,, ,,

centinormal $\left(\frac{N}{100}\right)$,, $\frac{1}{100}$,, ,, ,, or millinormal $\left(\frac{N}{1000}\right)$ containing $\frac{1}{1000}$ gram-equivalent weight per litre.

The gram-equivalent weight is the weight of the reagent expressed in grams, which will be required to enter into reaction with the equivalent weight of other substances, the equivalent weight of hydrogen being taken as 1·008. It always bears a simple relation to the molecular weight. Thus the equivalent weight of sodium hydroxide is equal to the molecular weight, that of sulphuric acid is half the molecular weight, that of potassium permanganate one-fifth of the molecular weight, and so on. The reason for the choice of these fractions is to ensure that a given volume of a normal solution of one reagent will react with an equal volume of a normal solution of another reagent. Thus since one molecule of sulphuric acid reacts with two molecules of sodium hydroxide according to the equation

$$H_2SO_4 + 2NaOH \qquad Na_2SO_4 + 2H_2O$$

and since a normal solution of the acid contains only half a gram-molecular weight per litre, whilst that of the alkali contains a whole gram-molecular weight per litre, it follows that a given volume of normal sulphuric acid will be neutralized exactly by an equal volume of normal sodium hydroxide.

Volumetric analysis is not directly applicable to the determination of all substances; the following are the chief cases where volumetric methods are useful:—

(*a*) The titration of *an acid by an alkali*, or vice versa; an indicator is added which undergoes a colour-change at the point of neutrality.

(*b*) The titration of a *reducing agent by an oxidizing agent* or vice versa. This method is of importance because it can be used for the determination of almost any metal which is capable of existing in more than one state of oxidation. Before commencing the titration, it is necessary to ensure that other metals of variable valency are absent, and also to ensure that the metal to be determined exists in the solution entirely in one state of oxidation. Usually the metal is brought to the lowest state of oxidation, and the solution is then acidified and titrated with potassium permanganate or potassium dichromate. The former requires no indicator, but cannot be used with accuracy in the presence of chlorides; the latter requires a side-indicator, unless the electrometric method is employed. Alternatively, the metal may be obtained in the highest state of oxidation, and allowed to react with potassium iodide; the amount of iodine set free is then determined by titration with sodium thiosulphate according to the equation :—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

In this titration the fading of the yellow colour due to iodine gives warning of the approach of the end-point ; but the colour is not pronounced, and before the iodine disappears completely, it is best to add a little starch solution, which produces a deep blue coloration as long as free iodine remains in the solution.

(c) A few volumetric methods depend on the *interaction of the two reagents to produce an insoluble salt*. Thus in a solution of a silver salt the silver may be estimated by titration with an ammonium thiocyanate solution, a drop of ferric salt being added as an indicator. As long as silver is present in excess in the solution, the thiocyanate is removed from solution as insoluble silver thiocyanate as quickly as it is added. But as soon as excess of soluble thiocyanate appears in the solution, a blood-red coloration due to ferric thiocyanate is produced, indicating that the end-point has been reached.

Quantitative Separation of Metals. Where the material under examination contains several metals, and it is desired to estimate these metals separately, some procedure must usually be adopted for separating these metals from each other. It is usually possible, by the addition of a chosen reagent, to precipitate certain metals completely, whilst the others remain in the solution. By a proper sequence of operations, it will be possible to separate each of the metals completely from the others, and when this has been accomplished the individual metals are precipitated in a suitable form (if not already precipitated in such a form during the process of separation) and weighed.

The quantitative separation of one metal from another is by no means so simple a matter as might be supposed from a mere study of the reactions of the individual salts. For example, if ammonium chloride and ammonia is added to a solution of a ferric salt, the iron is entirely precipitated as ferric hydroxide ; if the same reagents are added to a manganese salt solution, no precipitate is produced. It might be expected that if the reagents were added to a solution containing both ferric and manganese salts, the iron would be precipitated and the manganese would remain in the filtrate. This expectation, however, is not realized, since the ferric hydroxide seems to carry down manganese hydroxide with it. If a complete separation of iron and manganese is desired, it is necessary to redissolve the precipitate in acid, and then to repeat the precipitation once at least.

The methods of separating the individual metals from a mixture will depend somewhat on the nature of the metals present. But the general scheme adopted by all analysts consists in a separation of the metals into certain main groups, the separation being based on their varying behaviour towards certain simple reagents. The main groups into which the metals fall are given below, but the subsequent separation of the metals of a single analytical group from one another will not be considered at this point, being reserved for the analytical sections dealing with the individual metals in Volume II, III and IV.

(1) *Metals having oxides with very feeble basic properties*; these are either not brought into solution when the material to be analysed is extracted with dilute acid, or if held in solution through the presence of alkalis, are usually reprecipitated when the solution is weakly acidified and boiled:

Niobium, tantalum, tungsten.

(2) "*Noble*" *metals readily brought to the metallic state* by the action of reducing agents, and when in the metallic state undissolved by most acids:

Ruthenium, rhodium, palladium, osmium, iridium, platinum, gold.

(3) *Metals with sparingly soluble chlorides*, which are thrown down when hydrochloric acid is added to the solution:

Silver, mercury (in monovalent state). Also lead and thallium are partially precipitated from a cold solution.

(4) *Metals with sulphides* so *sparingly soluble* as to be precipitated by hydrogen sulphide even from *weakly acid* solutions.

(*a*) Those with sulphides insoluble in ammonium sulphide:

Copper, cadmium, mercury, lead, bismuth.

(*b*) Those with sulphides soluble in ammonium sulphide:

Molybdenum, germanium, tin, arsenic, antimony.

(5) *Metals precipitated* (usually as hydroxides) *on the addition of ammonium chloride and ammonia:*

Beryllium, aluminium, rare earths, titanium, zirconium, cerium, thorium, chromium (in trivalent state), uranium (in hexavalent state), iron (in trivalent state), gallium, indium.

(6) *Metals*, not precipitated by hydrogen sulphide in acid solution, but *having sulphides sufficiently insoluble* to be thrown down by the addition of ammonium sulphide to an *ammoniacal* solution:

Manganese, cobalt, nickel, zinc.

(7) *Metals having sparingly soluble oxalates*; precipitated by the addition of ammonium oxalate to a solution containing ammonium chloride and ammonia:

Calcium, strontium, barium.

(8) *Metals precipitated as a sparingly soluble phosphate* by the addition of sodium or ammonium phosphate to an ammoniacal solution:

Magnesium; also under certain circumstances, lithium.

(9) *Metals not precipitated by any of the reagents* mentioned above:

Sodium, potassium, rubidium, cæsium.

Determination of Atomic Weights. It is customary in works on chemistry to devote much space to the methods used for determining the accurate values of the atomic weights of the various elements. Recent research upon "isotopes" has tended to diminish the interest taken in the exact determination of these values, since it has been shown that all atoms—except hydrogen—have an atomic weight which, if oxygen is taken at 16·000, is an exact whole number; elements like chlorine (35·46), the accepted atomic weight of which lies far from a whole number, are found to consist of more than one species of atom, the weight of each individual species being an exact integer. Nevertheless a knowledge of the "mean atomic weights" arrived at by chemical methods remains of practical importance as a basis of our analytical calculations, and some reference must be made to the means adopted in their determination.

As early as 1865, Stas[1] carried out a series of careful and elaborate researches which led to a fairly accurate knowledge of the atomic weights of ten elements (Ag, Cl, Br, I, K, Na, Li, S, N and Pb); the numbers obtained for these elements have been used by later workers in the calculation of the atomic weight of other metals. Subsequent work has confirmed, on the whole, the substantial accuracy of Stas's investigations, but has led to slight alterations in the numbers accepted for the atomic weights of certain elements; the work of Richards in the revision of the atomic weights is worthy of special mention.

A short summary of Stas's method may be given. Potassium chlorate ($KClO_3$) was prepared in a state of great purity, and a weighed quantity of this salt was converted by heat to potassium chloride (KCl), elaborate precautions being taken to avoid loss by spurting or other causes. The chloride produced was weighed. The ratio of the weights

$$KClO_3 : KCl$$

enables us to calculate the molecular weight of potassium chloride (KCl), the atomic weight of oxygen being taken as 16·000.

In another series of experiments, Stas found the quantity of silver needed to precipitate the whole of the chlorine of potassium chloride as silver chloride. Very pure silver was prepared for this work, and a weighed quantity was dissolved in nitric acid; a weighed quantity of potassium chloride was then added, which was known to be just too little to precipitate the silver completely, and then a solution of potassium chloride of accurately known concentration was added from a special dropping pipette until the excess of the silver was removed. In this way the ratio

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[1] J. S. Stas "Œuvres Complètes" (Muquardt). A good summary is given by I. Freund, "Study of Chemical Composition" (Cambridge University Press).

$$\mathrm{KCl : Ag}$$

was obtained, and since the molecular weight of potassium chloride was already known, the atomic weight of silver was arrived at.

Stas also took weighed quantities of pure silver and converted them into silver chloride, bromide and iodide; the amount of these compounds was then obtained by weighing. The ratios $\mathrm{Ag : AgCl}$, $\mathrm{Ag : AgBr}$ and $\mathrm{Ag : AgI}$ were thus arrived at, and, the atomic weight of silver being known, the atomic weights of chlorine, bromine and iodine could be calculated.

The ratio $\mathrm{KCl : Ag}$ had already been determined, and the ratios $\mathrm{NaCl : Ag}$ and $\mathrm{LiCl : Ag}$ were obtained in the same way. The atomic weights of silver and chlorine being both known, the atomic weights of potassium, sodium and lithium followed.

Again, the increase of weight when silver is converted to silver sulphide, when lead is converted to lead sulphate, and when potassium chloride is converted to potassium nitrate (by evaporation with nitric acid) led to a knowledge of the ratios $\mathrm{Ag : Ag_2S}$, $\mathrm{Pb : PbSO_4}$ and $\mathrm{KCl : KNO_3}$.

From these ratios the atomic weights of sulphur, lead and nitrogen can be determined. In each case Stas was able to carry out alternative methods which enabled him to check the accuracy of the results obtained, and other methods have been employed by later experimenters.

The atomic weights of the other metals have been determined by methods not differing greatly in principle from those referred to above. One general method which has proved very valuable depends on the interaction of a chloride or bromide of the metal (sometimes a complex chloride or bromide) in a state of great purity, with a salt of silver. In some cases the weight of silver required to precipitate exactly the whole of the chlorine or bromine present is determined, yielding the ratio $\mathrm{MCl : Ag}$ or of $\mathrm{MBr : Ag}$. In other cases the silver chloride or bromide obtained is weighed, thus affording a knowledge of the ratio $\mathrm{MCl : AgCl}$ or of $\mathrm{MBr : AgBr}$. In either case the atomic weight of the element can be calculated from the ratio obtained.

Naturally, in the case of most elements, different workers using different methods have arrived at slightly different values for the atomic weight of a single element. Until recently an International Committee used annually to survey the research work accomplished during the previous year, and published a table of atomic weights giving the "most probable value" of the number in the case of every element. The discovery of isotopes has rightly caused an extension in the functions of this Committee.

In general the work of the determination of the atomic weight of any element may be divided into two main parts :—

(*a*) The preparation of the reagents in a state of great purity.

(*b*) The interaction of weighed quantities of these reagents under conditions which avoid all causes of error, and the isolation and weighing of the product obtained.

As an example which will serve to give some idea of the kind of precautions needed, a brief account of the re-determination of the ratio NaCl : AgCl by Richards and Wells[1] may be given. The details of the method were chosen with a view to avoiding certain errors which had entered even into the careful work of Stas on the same subject; much careful preliminary work was carried out in order to determine the conditions under which the various errors could be reduced to a minimum.

(*a*) Preparation of Pure Reagents.

Water. The traces of organic impurity in the distilled water of the laboratory were eliminated by redistilling from a weakly alkaline solution of potassium permanganate. Three distillations were performed, the final distillate being condensed and collected in platinum, and stored under conditions which excluded dust and acid fumes.

Sodium chloride was purified by precipitation from a concentrated solution with pure (redistilled) hydrochloric acid; the crystalline precipitate was separated from the mother liquor (which contains the impurities) by means of a centrifuge constructed of platinum. Before weighing, the sodium chloride was fused to expel moisture.

Silver. Recrystallized silver nitrate of considerable purity was treated with sodium chloride, and the silver chloride was filtered off from the mother liquor, which contained the main impurities. The chloride was then reduced by heating in a silver dish with a solution of invert sugar and sodium hydroxide (which had also undergone careful purification). The reduced silver was fused by means of a blast-lamp in a boat consisting of pure lime, and was allowed to cool down in the reducing flame; the button of almost pure silver obtained was then subjected to further purification, being made the anode of a small electro-refining cell containing silver nitrate solution made from the same almost pure silver. The cathode was a pure silver wire, and the very pure silver deposited on it was again fused, care being taken to prevent the access of oxygen before cooling, since oxygen is soluble in molten silver.

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[1] T. W. Richards and R. C. Wells, *J. Amer. Chem. Soc.* **27** (1905), 459.

(*b*) **Conversion of the Chlorine of Sodium Chloride to Silver Chloride.** Many of the operations were carried out in platinum vessels; in some cases silver, Jena glass, porcelain, or quartz ware was employed.

Freshly-fused sodium chloride was carefully weighed on a delicate balance in a specially designed balance-room, placed so as to possess a remarkably uniform temperature; carefully standardized weights were employed. The salt was dissolved in water, and the solution was greatly diluted (5 litres per mol.) in an Erlenmeyer flask. It was then precipitated with an excess of equally dilute silver nitrate (made from the pure silver mentioned above); the employment of dilute solutions was absolutely necessary for accurate work in order to avoid occlusion of silver nitrate or sodium chloride by the precipitated silver chloride. The precipitate was allowed to settle, and after standing for 15 hours it was washed by decantation, the wash water being poured off through a Gooch crucible lined with asbestos fibre, previously dried at 150° C. and weighed. The precipitate was washed three times with very dilute silver nitrate solution, and then six to nine times with pure water very slightly acid; finally it was transferred to the Gooch crucible. After washing was complete, the crucible was dried, the temperature being made to rise very slowly above 100° C. for two or three hours and kept at 150° C. for three hours more. It was then weighed, and afterwards the silver chloride was removed from the crucible, fused, and weighed again; the small loss of weight which was caused by fusion was due to minute drops of water entrapped and sealed in the hardened silver chloride.

Various corrections were applied. Minute amounts of chloride carried away by the wash water were estimated by an instrument called the nephelometer, which enables the cloudiness of the liquid under examination to be compared with that of a cloudy liquid prepared from standard solutions. Silver chloride is not quite insoluble in pure water, but the solubility is greatly reduced by the presence of excess of silver nitrate. If, therefore, the different portions of the wash water and filtrate are treated with silver nitrate, a cloudiness is produced, and the cloudy liquid can be examined in the nephelometer and the quantity of silver chloride removed in solution by the wash water can thus be allowed for. A small correction was also made for the minute amount of asbestos fibre carried through the crucible.

Ten complete analyses were made, using reagents obtained from different sources and purified in slightly different ways. The results of all ten experiments show a very remarkable agreement, ratio $\mathrm{AgCl} : \mathrm{NaCl}$ varying between 100 : 40·778 and 100 : 40·782.

VI. THERMO-CHEMISTRY [1]

Exothermic and Endothermic Changes. Most chemical and physical changes are accompanied by an evolution or absorption of heat-energy; those which involve an evolution of heat are called **exothermic**; those which cause an absorption of heat are called **endothermic.**

Interesting examples are afforded by the "latent heat" effects connected with simple physical changes. Heat is evolved when steam condenses to water, and is absorbed during the opposite process, the conversion of water to steam. In just the same way, the freezing of water is an exothermic change, whilst the melting of ice is endothermic. It is the absorption of heat by melting ice, which allows ice to survive for a considerable time in surroundings of which the temperature greatly exceeds 0° C.

The majority of chemical reactions which take place readily under ordinary conditions are exothermic; often the rise of temperature accompanying a change is very marked. The heat of combination of carbon with oxygen, a reaction upon which the maintenance of the temperature of most of our furnaces depends (directly or indirectly), may be quoted. Carbon unites with oxygen in two stages:—

$$2C + O_2 = 2CO + 58,000 \text{ cals.}$$
$$2CO + O_2 = 2CO_2 + 135,920 \text{ cals.}$$

The total heat-evolution is obtained by adding the two equations together:—

$$2C + 2O_2 = 2CO_2 + 193,920 \text{ cals.}$$
$$\text{or } C + O_2 = CO_2 + 96,960 \text{ cals.}$$

The figures quoted show that two-thirds of the total heat are evolved in the second stage. Consequently it is often convenient to use carbon monoxide (CO) as a gaseous fuel ("producer gas") for the heating of furnaces, in the place of solid coal.

The combination of most elements with oxygen results in an evolution of heat; when the heat development is sufficient to produce light, the process is termed **combustion.**

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[1] Much information on this subject is given in "Thermo-Chemistry," by J. Thomsen (Longmans, Green & Co.), from which source most of the values for the heat of reactions mentioned in this section are taken.

The heat of neutralization of strong acids by strong alkalis has already been alluded to. It can be expressed by the equation :—

$$H^{\cdot} + OH' = H_2O + 13{,}700 \text{ cals.}$$

Most anhydrous (water-free) salts (anhydrous calcium chloride, $CaCl_2$, for example) dissolve in water with the evolution of heat—a probable sign that combination between the salt and water actually occurs. Hydrated salts, such as $CaCl_2 6H_2O$, on the other hand, lower the temperature of the water in which they dissolve. Nor is this surprising, seeing that such solids contain more water than salt; the dissolution of hydrated calcium chloride has, indeed, been compared to the melting of ice.

Whilst most exothermic processes take place readily, endothermic processes, which involve an absorption of energy, are often difficult to bring about at ordinary temperatures. In homogeneous reversible reactions, where a balance between two opposing changes is possible, equilibrium is established at low temperatures only when the exothermic change is nearly complete. If, however, the temperature is raised the equilibrium gradually shifts, making possible the existence of a larger proportion of the "endothermic" bodies in the equilibrium mixture. Consider, for instance, the combination of oxygen and nitrogen, the two main components of air, to form nitric oxide (NO). The reaction is a balanced one :—

$$N_2 + O_2 \rightleftharpoons 2NO.$$

The formation of nitric oxide (NO) is, however, highly endothermic, and even at the high temperature of 1538° C. air contains—when a state of equilibrium has been reached—only 0·37 per cent. of nitric oxide. If we raise the temperature to 1922° C., however, 0·97 per cent. of nitric oxide can exist, whilst at 2402° C. the mixture contains as much as 2·23 per cent. of the endothermic gas.

The shifting of the equilibrium in the endothermic direction through the raising of the temperature is only one instance of what is known as **Le Chatelier's principle,** which can be stated in this way: If a system is in equilibrium, any alteration of the conditions will shift the equilibrium in such a sense as to oppose—and mitigate—the alteration in the conditions. Thus if we have nitrogen, oxygen and nitric oxide in equilibrium at, say, 1538°, and endeavour to raise the temperature, the equilibrium will be shifted in such a sense that more nitric oxide will be formed, and the heat absorbed in its formation will oppose—and partially nullify—our endeavour to raise the temperature.

The same principle can be applied to the shifting of equilibrium by change of pressure. Ice occupies a greater volume than the water from which it is formed. If we have a mixture of ice and water in equilibrium at 0° C. under atmospheric pressure, and we then apply an increase of pressure, the equilibrium is shifted and the ice begins to melt; this causes a decrease in volume, and opposes the attempt to increase the pressure. In other words, pressure lowers the melting-point of ice. In materials which are less bulky in the solid condition than in the liquid condition, increase of pressure raises the melting-point.

Free Energy and Internal Energy. All chemical and physical changes involve a passage from a reactive condition to a stable condition. Consider, for instance, any balanced reaction, of the type:—

$$A + B \rightleftharpoons AB.$$

If we start with the mixture of A and B, the mixture possesses reactivity—the power to react to form a certain amount of AB [1]; but, as AB is formed, and equilibrium is approached, the reactivity of the system diminishes, reaching a minimum when the equilibrium proportions are arrived at. On the other hand, if we start with the pure compound AB, this also possesses reactivity—the power to dissociate into A and B; but here again the reactivity of the system declines to a minimum as dissociation proceeds and the equilibrium proportions of A and B are approached.

Can we not find some means of expressing quantitatively these vague ideas of "reactivity" (the "tendency to react"), and of "affinity" (the "tendency to combine")? At one time certain chemists—impressed with the fact that *most* spontaneous changes were exothermic—thought that the evolution of heat accompanying a reaction was an appropriate measure of the "tendency to react." But such a view is in contradiction with the fact that numerous endothermic changes are known which occur spontaneously.[2]

It is now agreed that the "free energy" of a system is a suitable measure of the power to react. The free energy can be defined as the "maximum work" which can be done (at constant volume and constant temperature) by the system in coming to equilibrium; the free energy will clearly diminish as the system approaches equilibrium conditions. An example of how the "work" due to a chemical reaction can be obtained will be given shortly; for the present it is sufficient to state the general fact that a chemical or physical change will only occur spontaneously in such a direction as will cause a diminution of "free energy."[1]

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[1] The employment of the vague term "*reactivity*," used here in order to introduce the conception of free energy, has, of course, no connection with the employment of the word "activity," in chemical kinetics, in connection with certain molecules which have been "activated" by the absorption of radiant energy, or in some other way.

[2] A good criticism of the so-called Thomsen-Berthelot principle is given by W. C. McC. Lewis "System of Physical Chemistry" (Longmans, Green), Vol. II, pp. 340, 341 (1920 edition).

Sometimes a change takes place in stages, each stage corresponding to a diminution of free energy. Thus the reaction of chlorine with alkali can be made to take place in the following stages :—

$$\begin{aligned} 24NaOH + 12Cl_2 &\rightarrow 12NaOCl + 12NaCl + 12H_2O \\ &\rightarrow 4NaClO_3 + 20NaCl + 12H_2O \\ &\rightarrow 3NaClO_4 + 21NaCl + 12H_2O \\ &\rightarrow 6O_2 + 24NaCl + 12H_2O \end{aligned}$$

In this particular case, the decrease in the free energy is accompanied at each stage by a decrease in oxidizing power, which is well known to all who have used these reagents. We start with two highly reactive substances, chlorine and alkali, the former a most violent oxidizing agent. The first product, sodium hypochlorite, NaClO, is still a powerful oxidizing agent, although less powerful than free chlorine. The second product, sodium chlorate, $NaClO_3$ is somewhat less reactive, although still a moderately vigorous oxidizer. The third product sodium perchlorate, $NaClO_4$, is more stable still, and the final products, oxygen and sodium chloride, represent maximum stability and minimum free energy.[2]

How does this notion of free energy accord with the former crude, inexact, although often serviceable, conception that the magnitude of the heat-evolution accompanying a reaction is a measure of "eagerness" of the substances to react? For changes at constant volume, we can regard the heat evolution as being a measure of the diminution in the "internal energy" of the substances taking part in the changes. Now at very low temperatures, at which the equilibrium of a balanced reaction is practically at the exothermic end of the scale, the diminution in the "free energy" and in the "internal energy" attending the change will be almost equal. As the temperature (T) becomes higher, and the equilibrium is shifted in a direction favourable to the endothermic change, the diminution in free energy (A) and the diminution in internal water from which it is formed. If we have a mixture of ice and water in equilibrium at 0° C. under atmospheric pressure, and we then apply an increase of pressure, the equilibrium is shifted and the ice begins to melt; this causes a decrease in volume, and opposes the attempt to increase the pressure. In other words, pressure lowers the melting-point of ice. In materials which are less bulky in the solid condition than in the liquid condition, increase of pressure raises the melting-point.

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[1] An interesting paper by A. Korevaar, *J. Phys. Chem.* **25** (1921), 304, who points out that some physical chemists have used the term "affinity" to represent a force, and others to represent the work connected with a reaction, may be referred to.

[2] Compare W. Ostwald, "Principles of Inorganic Chemistry." Translation by A. Findlay (Macmillan).

Free Energy and Internal Energy. All chemical and physical changes involve a passage from a reactive condition to a stable condition. Consider, for instance, any balanced reaction, of the type:—

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[1] The employment of the vague term "*reactivity*," used here in order to introduce the conception of free energy, has, of course, no connection with the employment of the word "activity," in chemical kinetics, in connection with certain molecules which have been "activated" by the absorption of radiant energy, or in some other way.

[2] A good criticism of the so-called Thomsen-Berthelot principle is given by W. C. McC. Lewis "System of Physical Chemistry" (Longmans, Green), Vol. II, pp. 340, 341 (1920 edition).

Thermo-chemistry of Industrial Processes. Nearly all the changes with which chemical industry is concerned are difficult to bring about directly, for the simple reason that the minerals found on the earth have had plenty of time to complete the kind of changes which occur spontaneously; they are, therefore, singularly stable substances, which do not react with one another unless energy is supplied from outside. The most marked exception is coal, the combustion of which is the main source of the energy required for other reactions.

Since most of the metals evolve heat when they combine with oxygen, it is clear that the opposite process—the liberation of the metal from an oxide—would cause the absorption of heat. In the technical reduction of oxides to the metallic state, the oxide is usually heated with carbon, or with carbon monoxide, which combines with the oxygen and removes it from the metal. The combustion of carbon or carbon monoxide—if regarded by itself—would cause the evolution of much heat, and this fact reduces the endothermic character of the metallurgical process and may even render it exothermic.[1]

For instance, the simple decomposition of ferric oxide, the essential component of hæmatite iron-ore, into iron and oxygen, according to the equation

$$2Fe_2O_3 = 4Fe + 3O_2$$

would (if indeed it could be carried out at all at any temperature obtainable in an ordinary furnace) involve the absorption of 398,800 calories. But if the reduction is carried out by means of carbon monoxide, the combination of the carbon monoxide and the oxygen according to the equation

$$6CO + 3O_2 = 6CO_2$$

would cause the evolution of $3 \times 135{,}920$ cals. $=$ 407760 calories. Thus the combined metallurgical reaction

$$2Fe_2O_3 + 6CO = 4Fe + 6CO_2$$

will be mildly exothermic, the net evolution of heat being 407,760 − 398,800 = 8,960 calories.

Industrial processes involving the absorption of heat-energy are commonly carried out in furnaces at comparatively high temperatures. For highly endothermic changes such as the production of nitric oxide, the electric furnace, which puts extremely high temperatures at our disposal, has proved invaluable. The production of calcium carbide, which involves the absorption of about 116,000 calories per gram-molecule, is only possible in the electric furnace. The introduction of electrolytic methods (as opposed to electro-thermal methods) has, however, made it possible to conduct many reduction processes at ordinary temperatures, the energy being supplied, not as heat, but as electricity.

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[1] The thermo-chemical data collected in Chapter XI of Sir W. Roberts-Austen's "Introduction to the Study of Metallurgy" (Griffin) may be consulted with advantage.

VII. RADIATION

General. When a hot body is surrounded by other bodies at a lower temperature, it loses heat by "radiation"; the heat lost by the hot body is gained by those around it, and the process continues until the difference of temperature becomes imperceptible. Similarly if the central body is at a lower temperature than the surrounding objects, it will gain heat by radiation. Under equilibrium conditions, when the central body is at the same temperature as its surroundings, it can be regarded as losing and gaining heat at the same rate, with the result that no alteration of temperature occurs.

It is well known that some substances (those with **black** surfaces) absorb radiation well, whilst other bodies (those with bright surfaces) absorb very little, but reflect practically the whole of the radiation striking them. It might appear as a result that a black body surrounded by bright objects would necessarily come to a higher temperature than the latter. This, however, is not the case, because those surfaces which absorb heat most readily, also emit or radiate heat most completely. A black body is therefore the better radiator of heat than a bright body.

Since the heat of the sun reaches us after passing through millions of miles of space, it is evident that the transference of "radiant energy" does not depend upon the presence of matter along its path. It has for some centuries been thought that light-rays are a form of wave-motion, and gradually it came to be recognized that other kinds of radiation which do not affect the human eye are essentially similar in character. About 1888, the Hertzian waves—similar to those now used in Wireless Telegraphy—were produced by electro-magnetic means. They differed from the visible rays in having a vastly longer "wave-length," but moved with the same velocity (*in vacuo*); the general identity of the two kinds of radiation was gradually established. This gave support to the views previously advanced in 1865 by Clerk Maxwell, who believed that the visible rays have also an electro-magnetic character.

In 1895 Röntgen discovered the X-rays, a series which have a far shorter wave-length and higher frequency than the visible rays; they are produced when "cathode ray particles" (quickly moving electrons) strike against a metallic surface. It is now believed that X-rays are caused by the displacement of an electron belonging to one of the inner rings of the metallic atom ; possibly such an electron is knocked out of place by the cathode ray particle, and the energy liberated as the atom returns to its original condition takes the form of the emission of the X-ray. The X-rays can penetrate many substances which are not transparent to light ; hence their use in surgery. More recently they have been employed to detect flaws in the interior of metal castings with considerable success,[1] whilst, in the field of pure science, they have enabled such workers as W. H. and W. L. Bragg, Debye and Hull to obtain an insight into the structure of crystals, leading to the results which have already been discussed.

For the sake of clearness, a table is given below showing the wave-lengths and frequencies of various kinds of radiation.

Type of Radiation.	Wave-length (λ).	Frequency (ν).
Hertzian or "Wireless" Waves .	4 cms. to 10 kilos. (about 6 miles)	$7{\cdot}5 \times 10^9$ to 3×10^4
"Short Waves" used in Marconi System	300 metres	1×10^6
Infra-Red Waves (Invisible) . . .	Over $7{,}700 \times 10^{-8}$ cms.	Less than $3{\cdot}9 \times 10^{14}$
Visible Rays (approximate ranges only) :		
Red Rays . . .	$7{,}700 \times 10^{-8}$ to $6{,}470 \times 10^{-8}$ cms.	$3{\cdot}9 \times 10^{14}$ to $4{\cdot}6 \times 10^{14}$
Orange and Yellow Rays	$6{,}470 \times 10^{-8}$ to $5{,}500 \times 10^{-8}$ cms.	$4{\cdot}6 \times 10^{14}$ to $5{\cdot}5 \times 10^{14}$
Green Rays . . .	$5{,}500 \times 10^{-8}$ to $4{,}920 \times 10^{-8}$ cms.	$5{\cdot}5 \times 10^{14}$ to $6{\cdot}1 \times 10^{14}$
Blue and Violet Rays	$4{,}920 \times 10^{-8}$ to $3{,}600 \times 10^{-8}$ cms.	$6{\cdot}1 \times 10^{14}$ to $8{\cdot}3 \times 10^{14}$
Ultra-Violet Waves (Invisible). . .	Less than $3{,}600 \times 10^{-8}$ cms.	More than $8{\cdot}3 \times 10^{14}$
X-Rays and γ-Rays	$8{\cdot}4 \times 10^{-8}$ to $0{\cdot}07 \times 10^{-8}$ cms.	$3{\cdot}6 \times 10^{17}$ to $4{\cdot}3 \times 10^{19}$
Principal Palladium Line (Bragg) . .	$0{\cdot}576 \times 10^{-8}$ cms.	$5{\cdot}21 \times 10^{18}$

It will be noticed that the frequency increases as the wave-length diminishes. This is indeed a necessary consequence of the fact that all the waves move with the same velocity. For imagine (Fig. 14) a train of waves moving past a fixed point, P, with velocity v. The frequency (ν), that is the number of wave-

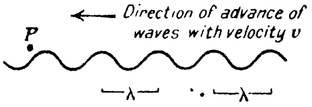

Fig. 14.

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[1] A general summary of the subject, with bibliography, is given by Sir R. Hadfield, *Trans. Faraday Soc.* **15** (1920), 1.

crests arriving at P each second, is clearly equal to $\frac{v}{\lambda}$, where λ is the wave-length, the distance from the peak of one wave to the peak of the next. Now the velocity, v, is the same for all waves moving through space, being equal to 299,940 kilometres per second. It follows that the frequency (ν) is inversely proportional to the wave-length (λ).

All the waves mentioned in the table above are capable of producing heat when absorbed by matter. Many of them, however, produce other effects far more striking. Those with wave-lengths shorter than about $5{,}000 \times 10^{-8}$ cms. cause the decomposition of silver salts, and therefore can be used in photography. Rays with wave-lengths between $7{,}700 \times 10^{-8}$ and $3{,}600 \times 10^{-8}$ cms. produce the sensation of light to the eye, the colour varying according to the frequency.

All solid and liquid substances, by virtue of the vibrations of the atoms or electrons, are capable of sending out radiation, but at low temperatures the waves are of too small a frequency to affect the eye. As the temperature rises, however, and the movement becomes more violent, waves of increasingly high frequency are produced along with those of low frequency, and, at about 515° C., all solid substances begin to glow with a dull red heat; at higher temperatures, they become bright red, and finally at very elevated temperatures, they attain "white heat." So long as the material in question is a *black* (non-transparent) body, the proportion of different wave-lengths present in the light emitted depends only on the temperature; in other words, all "black bodies" at a given temperature have the same "emission spectrum." This is not the case if the body is transparent to radiation of any particular wave-length. An explanation of the distribution of wave-lengths in the spectrum of a black body, and its variation with the temperature, is afforded by Planck's "quantum theory," which will be referred to at a later stage.

Refraction and Reflection of Light on passing from one Medium to another. In general, when light-waves pass from one medium to another, they suffer a change of direction; short waves are deflected more than long waves. The amount of the angular deflection depends on the angle at which the rays strike the boundary between the media, and also upon the nature of the media.

It is possible to assign to every material a number called the "**refractive index.**" When light passes from one material to a second material whose refractive index is very different from that of the first, it is likely to suffer a considerable deflection.

Where, however, the second medium has a refractive index nearly the same as the first, there will be a much smaller change of direction. If the refractive indices of the two media be μ_1 and μ_2 respectively, and if a light-beam before striking the surface separating the media makes an angle of θ_1 with the line perpendicular to that surface, and after suffering "refraction," makes an angle θ_2 (see Fig. 15),

$$\text{then} \quad \sin\theta_2 = \frac{\mu_1}{\mu_2}\sin\theta_1$$

When the two media have the same refractive index, so that $\mu_1 = \mu_2$, it follows that $\theta_1 = \theta_2$; in other words, there is no alteration in the direction of the light-beam. In any case there is no alteration in direction, when the light falls in a direction perpendicular to the interface, for then both θ_1 and θ_2 are equal to zero.

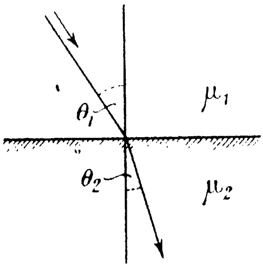

Fig. 15.—Deflection of a Ray on passing from one Medium to another.

Upon the change of direction of light, passing from one medium to another is founded the principle of the microscope, the telescope, the spectroscope, the camera and practically all optical instruments; to the optician a knowledge of the refractive index of a glass is of the first importance. As a rule, heavy glasses, containing lead and barium, have a higher refractive index than glasses containing only the lighter metals.

But there is another equally important phenomenon which occurs when light passes from one medium to a second; a certain fraction of the light is reflected at the interface. The fraction reflected is always small, but is in general greater when the refractive indices of the two media differ greatly than when they are close together. When a thin slab of glass is placed, for instance, on a wooden table, the amount of light reflected at the surface is but trifling; the wooden surface will still be seen through the glass, the presence of which may easily escape observation. But if, instead of the slab of glass the table is covered with a layer of glass powder of the same thickness, the effect is quite different. The light now has to pass across hundreds of glass-air interfaces before it reaches the wood, and, although the amount reflected from each interface is trifling, the aggregate reflection is very considerable. The whole surface appears white, and the wood below is completely hidden. If, now, the glass powder is wetted with water, the reflection is diminished, for the refractive index of water is nearer to that of glass than is the refractive index of air; the powdered glass appears to have recovered some of the transparency of the solid plate. If, instead of water, the glass is wetted with cedar oil, which has a refractive index quite close to that of glass, the reflection diminishes still more, and the colour of the wood below is easily seen.

Now when a coat of paint is put on wood or metal, the coating consists of a large number of transparent particles of pigment suspended in a film of dried oil (the " vehicle "). Light passing through a film of this kind is reflected wherever it passes into, or out of, a pigment particle. In order to obtain satisfactory reflection of the light by means of a thin coat of paint, it is necessary to choose a pigment whose refractive index is very different from that of the vehicle.

Nearly all practically useful pigments are heavy substances—compounds of lead, zinc or barium—which have high refractive indices, greatly exceeding that of the vehicle. Substances with low refractive index have small "**covering power**," or, as it is sometimes called, " hiding power " ; a comparatively large quantity of such a substance is required to prevent the wood or metal below from showing through the film. Another requirement of a pigment of good covering power is evidently that it should exist in a fine state, so as that light penetrating the paint-coat meets a large number of oil-pigment boundaries before it can reach the wood or metal below.

Whilst the light striking the surface of a transparent substance like glass suffers but little reflection, the reflection at the smooth surface of an opaque substance, e.g. a metal, is considerable. The law governing the direction of the reflection of light at a plane surface is a very simple one ; the ray after reflection remains in the plane containing the incident ray and the line drawn normal to the surface at the point of incidence, and makes the same angle with that line as does the incident ray.

Continuous Spectra and Line Spectra. By means of a spectroscope, the light proceeding from a hot body can be analysed. For the purposes of a chemist, a prism-spectroscope is quite convenient, although the physicist often prefers an instrument fitted with a diffraction grating. A glass prism causes all waves striking upon it to be deflected in their course, but the short rays are more deflected than the long rays, and the rays of different wave-lengths are thus separated from one another. If the light from a white-hot solid is examined, a "**continuous spectrum**" is seen, consisting of red at one end, passing insensibly into orange and yellow, which in turn passes into green, and from green into blue and violet.

This continuous spectrum shows that "white light" contains rays of all the wave-lengths to which the eye is sensitive. If, however, in the place of a solid, we use a glowing gas as the source of light, we usually obtain—not a "continuous spectrum"—but a "**line spectrum.**" The visible spectrum of a flame containing sodium vapour appears to be a single yellow line (the "D line"), which, in a spectroscope of high dispersive power, may be found to be really a pair of lines very close together; actually the complete sodium spectrum contains more than this one pair of lines, but only the "D" pair falls on to the part of the spectrum visible to the eye. The pair correspond to wave-lengths of $5{,}896 \times 10^{-8}$ and $5{,}890 \times 10^{-8}$ cms.[1]

If we pass the light from an intensely hot solid body through a flame containing sodium vapour at a lower temperature, we obtain the usual bright continuous spectrum of the solid body, but—at just that place where the yellow line of the sodium spectrum should fall—we obtain a line which, compared to the rest of the continuous spectrum, is extremely dark. This is easily explained. The sodium vapour is a specially good radiator of rays of wave-lengths $5{,}890 \times 10^{-8}$ and $5{,}896 \times 10^{-8}$ cms.; it follows, therefore, that it will also have a strong absorptive power for the same rays; consequently it has extracted light of these particular wave-lengths from the continuous spectrum of the hot solid, with the production of the dark line. Numerous dark lines occur in the otherwise continuous spectrum produced by the light from the sun; one of them corresponds in position to the D line of sodium, and therefore we know that sodium occurs in the sun. In exactly the same way, the presence in the sun of numerous other well-known elements has been detected.

Spectrum Analysis. The spectroscope is extremely useful in chemical analysis for the recognition of metals in a salt-mixture, especially for metals of Groups IA and IIA, all of which yield well-marked lines. Very small quantities of the elements can be recognized, such as would be difficult to detect in any other way. In searching for one of these metals, it is usually sufficient to moisten the substance to be tested with hydrochloric acid, to introduce it into a colourless flame and to observe the result in a spectroscope. If, however, it is desired to look for one of the less volatile metals, a higher temperature (e.g. that of the electric arc) must be used in order to vaporize the metal in question.

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[1] The cause of the emission of radiations of certain definite wave-lengths by substances in the gaseous state, and the conclusions regarding atomic structure which have been founded upon the study of line spectra, is too large a subject to be discussed here. Reference should be made to the papers of N. Bohr, *Phil. Mag.* **26** (1913), 1, 476; **27** (1914), 506; *Zeitsch. Phys.* **9** (1922), 1. Sir J. J. Thomson, *Phil. Mag.* **36** (1920), 419. J. W. Nicholson, *Trans. Chem. Soc.* **115** (1919), 855.

If a spectroscope is not at hand, the colour of the flame alone sometimes allows the chemist to judge of the nature of the substances introduced into it. Sodium salts give a yellow flame, potassium salts a purple flame, barium salts a green flame, and so on. The simple "flame tests" are, however, somewhat uncertain; several metals, for instance, give red flames which—unless viewed through a spectroscope—may be mistaken for one another. Moreover if a mixture contains much sodium, the yellow colour produced is likely to mask the effect of the other metals.

Absorption Spectra. The natural colour possessed by many substances at ordinary temperatures is generally due to the fact that the substances display selective absorption of the light passing through them. A solution of potassium permanganate, for instance, absorbs some of the yellow and green rays of sunlight very completely, whilst allowing the red, blue and violet rays to pass without much loss; it possesses consequently a reddish-violet colour.

By viewing the light which has passed through a coloured solution in a spectroscope, the "**absorption spectrum**" can be studied. Thus a solution of potassium permanganate shows five fairly sharp absorption bands in the yellow and green. All the permanganates—including permanganic acid—show the same bands within exactly the same limits, a fact that suggests that they are due to the $(MnO_4)'$ ion, or possibly to the (MnO_4) group.[1]

Nearly all the metals with brightly-coloured salts occur in the central portion of the periodic table, although colour is also met with in the group of the rare earths. The power of selective absorption seems in general to be connected with variable valency; metals with fixed valency have usually colourless salts. Variable valency suggests that the arrangement of electrons in the outer shell, or ring, of the atom is capable of variation, and that the restraints holding the electrons in their positions are probably smaller than in atoms of fixed valency. Consequently, these electrons can be displaced by light of comparatively low frequency (i.e. visible light), and such light is consequently absorbed, giving rise to colour. On the other hand, in atoms of fixed valency, the restraint holding the electrons in position is so great that the electrons can only be displaced by light of high frequency; selective absorption in the invisible ultra-violet region may occur, but this will not, of course, produce colour in the ordinary sense of the word. It is noteworthy that in several metals most of the salts are colourless, but one or two exceptional compounds have a yellow tinge. For instance, most of the silver salts are colourless to the human eye, because the selective absorption which occurs lies in the ultra-violet region beyond the limit of visibility. But in the case of the iodide, the absorption extends a little farther in the direction of low frequency, and visible blue rays are absorbed also; consequently silver iodide has a yellow colour.[1]

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[1] See W. Ostwald, *Zeitsch. Phys. Chem.* 9 (1892), 583, but also T. R. Merton, *Trans. Chem. Soc.* 99 (1911), 637. Compare A. H. Hantzsch, *Ber.* 41 (1908), 1216, 4328; *Zeitsch. Phys. Chem.* 72 (1910), 362.

The study of an absorption spectrum is occasionally useful to identify a metal in a solution containing various salts. Some of the rare earth metals, notably neodymium and prasiodymium, have very characteristic absorption spectra; the separation of these metals from others of the group, and from one another, can conveniently be regulated by the aid of the spectroscope.

In most cases where the colour of a solid substance *appears* to be due to light reflected from the surface, closer investigation shows that part of the light actually sinks some way into the substance before it is reflected, and therefore suffers selective absorption. For instance, when light strikes a heap of loose powdered lead chromate, many of the rays penetrate several grains before being reflected from some chromate-air interface within the heap. During the passage through the pigment, blue rays are absorbed more than others, and the emergent light has, as a whole, a yellow colour. The colour will be more intense if the powder consists of coarse grains than if it consists of fine particles, since in the first case the light will penetrate through a greater thickness before being reflected. Similarly large crystals of copper sulphate are distinctly blue, but when ground in a mortar yield a powder which appears nearly colourless.

Surface Reflection. As opposed to the coloration due to *selective absorption* of light which penetrates *through* the substance, some materials possess a characteristic colour due to *selective reflection at the exterior surface.* Usually the substance reflects with especial ease those rays which it absorbs, and the colour due to surface reflection is often roughly complementary to that caused by absorption. Thus the dye fuchsine, which absorbs green rays, has a magenta colour when viewed by transmitted light; but its surface possesses a brilliant green lustre. There are, however, many exceptions to this rule; the dye, cyanine, for instance, has a purplish colour whether viewed by reflected or transmitted light.

The colour due to surface reflection is best shown by metals.

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[1] This view of the connection between colour and valency is developed by G. N. Lewis, *J. Amer. Chem. Soc.* 38 (1916), 783. Compare N. Bohr, *Zeitsch. Phys.* 9 (1922), 52.

If gold is beaten out into leaf thin enough to be transparent, its colour, when viewed by transmitted light, is green, or, if the leaf is made extremely thin, blue. These colours are due to the fact that the red and yellow rays of the light passing through it are absorbed. Yet gold viewed by reflected light is, as is well known, yellow; if the light is reflected several times at gold surfaces, the oft-reflected ray has a distinctly red hue. The colour is here caused by selective reflection; gold leaf reflects 90 per cent. of the red rays that impinge on it, but only 50 per cent. of the green ones.[1]

It is rather interesting to note that a colloidal solution of gold, consisting of minute particles of metal suspended in water, shows an exactly opposite colour-effect; instead of appearing green by transmitted light and red by reflected light, the solution is red by transmitted light and green by reflected light. Ruby glass, which consists of minute particles of gold suspended in glass, is also deep red when viewed by transmitted light. The reversal of the normal coloration is due to the small size of the particles, but the explanation is somewhat complicated, and those interested must study it elsewhere.[2]

It is worth while to notice that the colour of colloidal solutions varies somewhat with the size of the particles, and changes if they join to one another to form "secondary aggregates." On adding sodium chloride to the red solution of gold, the minute particles join together to form loose clusters, and the colour of the solution, viewed by transmitted light, becomes blue.

Many metals which appear bright when obtained in the compact state with a smooth, polished surface appear dark when present in a porous, furry condition. Thus platinum foil is bright and glittering, but "reduced" platinum is a black powder. The foil reflects much of the light striking it directly into the eyes of the observer; but the light striking the reduced metal is probably repeatedly reflected from between the sides of the channels threading the porous mass, and suffers loss of intensity at each reflection until gradually it comes to be almost entirely absorbed.

Interference Colours due to thin Films. Another type of coloration of great importance in the study of metals is caused by the presence of a thin film upon a reflecting surface. It is well known how copper, when heated in air to different temperatures, shows all sorts of beautiful tints in different places, the tint depending on the temperature, and the time of exposure. The same phenomenon is noticeable in the case of iron heated in air, and the colour produced is used—in the tempering of steel—to gauge the temperature of the metal. Tints are also seen on polished silver which has been exposed to hydrogen sulphide.

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[1] See R. W. Wood, "Physical Optics" (Macmillan, 1911), p. 487. R. Schenck, "Physical Chemistry of the Metals"; translation by R. S. Dean (Chapman & Hall), pp. 27, 28.

[2] A simplified treatment of the matter is given by W. D. Bancroft, *J. Phys. Chem.* **23** (1919), 554.

Now these effects are caused by the appearance of a very thin film of oxide—or, in the last case, sulphide—on the surface of the metal[1]; the colour produced depends mainly on the thickness of the film. Consider (Fig. 16, case (*a*)) light reflected from a double surface of this kind. Let one ray of light (EF) be deflected from the oxide-air interface, and another ray (CD) from the metal-oxide interface, the emergent rays (DG and FG) following the same path. Now, if the wave-length of the light and the angle of incidence is suitable, the rays reflected from the two interfaces will both be in the "same phase," the crests of one ray corresponding to the crests of the other, as suggested in the diagram.[2] As a result the two rays

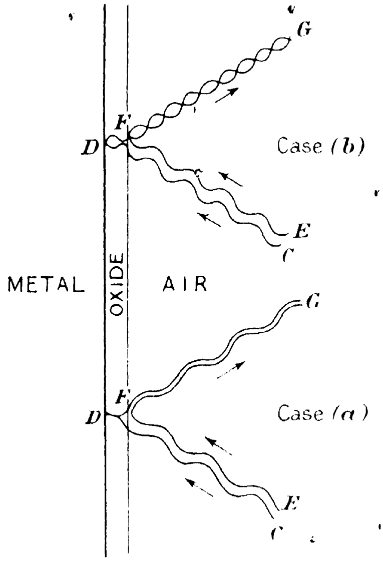

FIG. 16.—Production of Colour by Thin Films.

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[1] Possibly not an oxide or sulphide of definite composition. See U. R. Evans, *Trans. Faraday Society*, **18** (1922), 6.

[2] It is assumed that the film of oxide or sulphide has a refractive index intermediate between that of the metal and air. In such a case the difference of phase is given by the "difference of path" alone. See R. W. Wood, "Physical Optics" (Macmillan, 1911), p. 170.

of light unite to form a ray of greater intensity. If, however, the wave-length is changed, the angle of incidence and thickness of film remaining the same, as in Fig. 16, case (*b*), the emergent rays may be in opposite phases, the crests of one ray corresponding to the troughs of the other. In this case, the two portions will "interfere" or cancel one another. Evidently, therefore, when white light falls on a double surface of this kind, certain wave-lengths will be extinguished in the reflected portion, whilst other wave-lengths will be reflected with considerable intensity, and thus the reflected light will no longer be white, but distinctly coloured. If the thickness of the film be altered, or even—in some cases—if the angle at which the surface is viewed be altered, the wave-lengths of the light extinguished will be changed, and the consequent "colour" of the film will be changed also.

The very beautiful colours seen when light falls upon water covered with a thin film of oil are due to a similar cause as those produced by oxide films.

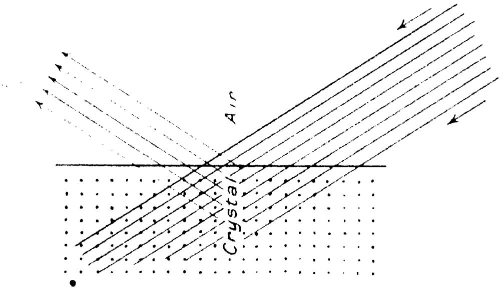

Fig. 17.—Reflection of X-rays from the Layers of Atoms within a Crystal.

X-Ray Analysis of Crystal Structure. It has been repeatedly stated that the atoms of a crystal are arrayed in definite layers. The distance between two layers is very small compared even with the wave-length of light. It is, however, comparable to the wave-length of an X-ray, and advantage has been taken of this to obtain a series of phenomena somewhat analogous to the one just described.

If a train of X-rays (Fig. 17) passes through a crystal, it meets with the parallel ranks of atoms, and from each rank of atoms a certain amount of reflection occurs. The amount reflected from each rank is very small, but, if the reflected rays are all in the same phase, the cumulative reflection will be sufficient to produce a marked effect on a photographic plate. The fulfilment of the condition that the reflected rays shall all be in one phase will depend upon the wave-length of the rays employed, the angle of incidence and the distance between the ranks of atoms. For X-rays of a given wave-length there will be certain particular angles of incidence which will produce very marked reflection, the intervening angles, causing very little reflection. By observing these angles of maximum reflection on different faces of a crystal, we can calculate the distances between the layers of atoms parellel to different faces of the crystal, and, in this way, information as to the packing of the atoms in the crystal is arrived at.[1]

The results obtained by these methods are of the greatest importance and many of the statements regarding crystal-structure which have already been made in this book are founded upon them.

Photo-Chemistry. It has already been stated that radiations of wave-lengths shorter than about $5{,}000 \times 10^{-8}$ cms. can cause the decomposition of certain silver compounds. Many other substances are decomposed by the action of light; for instance, some of the salts of iron and uranium. The combination of chlorine and hydrogen gas does not take place in the dark, but takes place with great violence if sunlight is allowed to fall on the mixture. All these reactions are said to be "photo-chemical." Another similar change which has already been mentioned is the production of free electrons when ultra-violet light is allowed to fall on the surface of a metal (the so-called "photo-electric effect").

Now in every case it is necessary that the light shall be of sufficiently high frequency. Violet or ultra-violet rays are active in decomposing a silver salt, whilst red light—as every photographer knows—is without action. In the case of the "photo-electric effect" a definite frequency exists for each metal below which the light—however intense—is entirely without action upon the metal.

This interesting fact—like many other facts connected with radiation—is best considered in the light of the **Quantum Theory.**[2] According to one form of that theory, radiant energy is not given out by an atom or molecule in random quantities, but in definite parcels, or "**quanta**"; according to another form of the theory, it is only absorbed in "quanta." In general, one quantum will be absorbed—or emitted—by each molecule; conceivably, in certain cases, two, three or four quanta may be absorbed—or emitted—

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[1] The method of deriving the information is explained in a simple manner in W. H. and W. L. Bragg's "X-Rays and Crystal Structure" (Bell).

[2] M. Planck, *Ber. Deutsch. Phys. Ges.* **2** (1900), 237; *Sitzungsber. Preuss. Akad.* (1914), 918. A. Einstein, *Ann. Phys.* **17** (1905), 132; **20** (1906), 199. See also W. C. McC. Lewis, "System of Physical Chemistry," Vol. III (Longmans, Green). J. H. Jeans, *Trans. Chem. Soc.* **115** (1919), 865.

but never a fraction of a quantum. The value of the quantum is, however, not the same for all kinds of radiant energy, but varies with the frequency ν, being equal to $h\nu$, where h is a number known as Planck's Constant. If the unit of time employed in expressing the frequency is the second and the unit of energy adopted is the erg, Planck's constant has a value of $6{\cdot}5 \times 10^{-27}$.

Let us now return to the production of free ions by the action of light on a metal. If a quantity of energy, q, is needed to remove one electron from an atom on the metallic surface and if this quantity is to be supplied as radiant energy by the absorption of one quantum, then that quantum $h\nu$ must clearly be equal or greater than q. In other words, ν must be equal or greater than $\frac{q}{h}$. It follows that if the frequency is less than a certain critical value, the radiation is without effect. In a similar way, it is possible to explain the fact that only light of very short wave-length causes the decomposition of silver salts, although here the question is somewhat more complicated.[1]

The quantum theory, originally introduced to explain the distribution of wave-lengths in the light emitted by a hot body, is now being applied with success to such subjects as catalysis, which at first might appear to have little to do with radiant energy. The theory, however, suffers under the disadvantage of being without an accepted physical basis. As long as the chemist is without a clear picture which will enable him to understand *why* energy should necessarily be sent out through space "tied up in bundles of amount $h\nu$," the theory will not become useful in the way that the atomic theory is useful. It is possible that certain suggestions recently made by Langmuir [2] may lead ultimately to the provision of the "physical basis" which is so badly required.

The Application of Photo-Chemical Conceptions to ordinary Chemical Reactions. An interesting hypothesis has been put forward by Lewis,[3] who suggests that ordinary chemical reactions, which proceed as readily in the dark as in the light, are really in a sense photo-chemical, but depend upon the absorption of the relatively long, invisible, infra-red rays, such as are emitted by substances at ordinary temperatures. This theory provides an explanation for the remarkable increase in the velocity of all ordinary chemical reactions caused by a comparatively small rise of temperature—a fact which is very difficult to explain in any other way; the increase of temperature causes a marked increase in the "radiation density" of the radiation in question—which increase is sufficient to account for the increased reactional velocity. According to this theory, a catalyst, if added, aids the reaction by emitting radiation of the desired type, and thus acts in the same way as an increase of temperature. The theory is perhaps rather more successful in explaining homogeneous catalysis than in its application to heterogeneous catalysis.[1]

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[1] See J. Stark, *Phys. Zeitsch.* **9** (1908), 892, 894. M. Bodenstein, *Zeitsch. Phys. Chem.* **85** (1913), 329. E. Warburg, *Sitzungsber. Preuss. Akad.* (1911), 746; (1912), 216; (1913), 644; (1914), 872; (1915), 230; (1916), 314; (1918), 300, 1228; (1919), 960. Compare I. Langmuir, *Trans. Amer. Electrochem. Soc.* **29** (1916), 147.

[2] I. Langmuir, *Phys. Rev.* **18** (1921), 104.

[3] A. Lamble, and W. C. McC. Lewis, *Trans. Chem. Soc.* **105** (1914), 2330; **107** (1915), 233. W. C. McC. Lewis and others, *Trans. Chem. Soc.* **109** (1916), 796; **111** (1917), 457, 1086; **113** (1918), 471; **115** (1919) 182, 710, 1360; **117** (1920), 623; **121** (1922), 665. E. K. Rideal and J. A. Hawkins, *Trans. Chem. Soc.* **117** (1920), 1288.

Fluorescence and Phosphorescence. When light falls upon certain substances, they commence to give out light of a colour different from that of the light which is falling upon them; usually the emitted light has a frequency lower than that of the incident light. Such substances are said to be "fluorescent." Good examples of fluorescence are afforded by solutions of uranium salts. Sodium vapour is also fluorescent. Since the emitted light is not necessarily sent out in the direction in which the incident light was travelling, a "scattering" of the light is produced; the phenomenon of fluorescence is best observed if the eye is placed so that the incident light cannot reach it directly, but only the light emitted by the fluorescent substance. There is little doubt that in the case of the salts of hexavalent uranium, the light energy absorbed by certain molecules produces some endothermic change, and that the next moment the reverse change occurs, the original hexavalent salt being regenerated and the energy being re-emitted as visible rays.[2]

The phenomenon of **phosphorescence** is similar to that of fluorescence, but a phosphorescent substance continues to glow for an appreciable time after the light has ceased to beat upon it. It is probable that all *solid* fluorescent substances are really phosphorescent, although in some cases the glow may only persist for a fraction of a second after the exciting light has been shut off.

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[1] Compare W. D. Bancroft, *Trans. Amer. Electrochem. Soc.* **37** (1920), 21.

[2] E. Baur, *Schweiz. Chem. Zeit.* **2** (1918), 40. Abstract, *J. Chem. Soc.* **114** (1918), ii., 143.

VIII. GEO-CHEMISTRY[1]

Early History of the Earth. Many millions of years ago, a quantity of matter—probably in the gaseous condition—was thrown off from the sun; this matter divided into various fragments, which became the different planets. The fragment with which we are most concerned again divided into two unequal parts, one of which is now called the Earth and the other the Moon.[2]

At the time of this division, the matter composing the Earth had probably cooled down to a considerable extent, and was probably already largely in the liquid state. Afterwards, when it had cooled still further, a solid crust appeared on the surface. All cooling is accompanied by shrinkage, and presumably the exterior portions, which cooled most quickly, tended to shrink more than the interior. The unequal shrinking—aided, no doubt, by other causes—occasioned violent earth-movements which, in a greatly lessened degree, persist to the present day. In some places those movements would show themselves by the upheaval of the surface to form mountain-chains. In other localities, the crust would break, and the still molten interior of the earth would spurt forth vast floods of lava; indeed, compared to the early volcanic activity of the earth, our modern eruptions must be regarded as very trifling affairs.

Denudation. At the time of which we have been speaking, the "atmosphere" or gaseous envelope which surrounded the crust, must have contained, besides the oxygen and nitrogen which remain to the present day in the gaseous condition, much water-vapour and probably a considerable amount of carbon dioxide. An important date in the history of the earth was clearly reached when the temperature became sufficiently low to allow the condensation of water in liquid form, with the consequent production of seas in the lower portions of the earth. The local variations of temperature, however, allowed evaporation to commence over the seas, and the subsequent condensation upon the mountains (the phenomenon which we now call "rain") gave rise to streams and rivers flowing down into the sea. This gradual passage of water from high places to low ones was not without its effect upon the primitive rocks of the earth, which became both mechanically disintegrated, and chemically attacked, by the water flowing over them. Later on, when the temperature became suitable for the appearance of life, the roots of plants and the burrowing of animals assisted in the task of breaking up the rocks, whilst the presence of organic acids—as well as of carbon dioxide—in the water aided in the chemical erosion of the same materials. Thus a process of "denudation," a constant wearing down of mountains, accompanied by the continuous transport of material to the sea, commenced, and the same process persists to the present day. The insoluble matter brought down by the rivers was deposited on the sea-bottom, and, when subsequently fresh earth-movements pushed up the sea-bed to form new land, the sediments were consolidated into rock. We see, thus, the appearance of a fresh type of rock, the **Sedimentary Type.** Of course, as soon as a sedimentary rock is pushed up above the surface of the sea, the restless forces of denudation commence to wear it down, just in the same way as the original crust was worn down before. But, in spite of this rapid denudation, there exist to-day vast masses of sedimentary rocks, some of which were probably laid down at least 500,000,000 years ago.

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[1] The following books may be consulted with advantage: "Mineral Deposits," by W. Lindgren (McGraw-Hill); "Ore Deposits," by F. Beyschlag, J. H. L. Vogt and P. Krusch (translated by S. J. Truscott, Macmillan). "Geochemistry," by F. W. Clarke (U.S. Geol. Surv.); "Geology of Ore Deposits," by H. H. Thomas and D. A. Macalister (Arnold).

[2] H. Jeffreys, *Roy. Astr. Soc. Notices*, **78** (1917–18), 116, 424.

Main Epochs in the Geological History of the Earth. As it will be necessary to refer occasionally to the ages of different rocks and ores, it is convenient to give (on opposite page) a table showing the names generally used by geologists for some of the main periods of geological time, the oldest being shown first. The periods mentioned were by no means equal. The first or Pre-Cambrian epoch was probably almost as long as all the others put together. Studies of radioactive minerals occurring in rocks of this age seem to suggest that it lasted from about 1,600,000,000 to about 1,000,000,000 B.C. Similar evidence suggests that some of the Carboniferous rocks were in process of formation about 340,000,000 years ago.[1] Such numbers are quoted merely to give some measure of the ages involved, and should not be regarded as rigidly accurate.

Intrusion. From time to time, as shown in the table, important earth-movements have occurred, as a result of which fresh masses of fused material (rock-magna) have been pushed up from the hot interior of the earth into the sediments composing the crust. Wherever this "igneous" material actually reached the surface, it was poured forth as a lava-stream and cooled rapidly. Owing

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[1] A. Holmes, *Proc. Roy. Soc.* **85** [A] (1911), 256. Compare estimates of the age of the crust by H. N. Russell, *Proc. Roy. Soc.* **99** [A] (1921), 84.

Main Periods of Geological Time.

	Pre-Cambrian	(*Archæan* system of earth-movements at this time)
Palæozoic	Cambrian	
	Ordovician	
	Silurian	
	Devonian	(*Caledonian* system of earth-movements at this time)
	Carboniferous	
	Permian	(*Hercynian* system of earth-movements about this time)
Mesozoic	Triassic	
	Jurassic	
	Cretaceous	
Cainozoic	Tertiary	(*Tertiary* system of earth-movements at this time)
	Recent	

to the rapid cooling, the "volcanic rocks" produced were of a more or less **glassy** character. The main portions of the molten mass, however, have generally failed to reach the surface, and have solidified very slowly some way below the surface of the crust; this slow cooling gives rise to a **crystalline** type of rock, of which granite is a familiar example. In many regions of the earth, vast masses of crystalline rock which originally hardened far below the surface are now exposed, owing to the removal of the material above by the process of denudation.

Before a more detailed description of the different types of rock is possible, some idea must be given of the composition of the magma, from which directly or indirectly most of the materials of the present crust of the earth have been derived. If we may judge from analyses of the crystalline rocks which are accessible to us, the magma may be described as being made up mainly of "silicates of aluminium, iron, calcium, magnesium, potassium and sodium." Silicates of these six metals, indeed, account for about 98·6 per cent. of the composition of visible igneous rocks; all the other known elements can be regarded—for the moment—as mere "minor constituents." It is quite probable that the material composing the centre of the earth is of a different character—possibly consisting of an iron-nickel alloy; but the composition of the material forming the central core of the earth is not of great importance for our present purpose.

Silicate Minerals. The **silicates** are salts produced by combination of silica (SiO_2) with metallic oxides in different proportions. They are a very large family, but can in most cases be regarded as derived from one of the following silicic acids through the replacement of hydrogen atoms by atoms of metals :—

Trisilicic acid, $2H_2O.3SiO_2$ or $H_4Si_3O_8$, giving **trisilicates** such as orthoclase, $KAlSi_3O_8$.

Metasilicic acid, $H_2O.SiO_2$ or H_2SiO_3, giving **metasilicates** such as enstatite, $MgSiO_3$.

Orthosilicic acid, $2H_2O.SiO_2$ or H_4SiO_4, giving **orthosilicates** such as zircon, $ZrSiO_4$.

The two last examples chosen are simple silicates which may contain only one metal. Orthoclase, on the other hand, is a double silicate, containing two metals, the potassium atom replacing one hydrogen atom of the $H_4Si_3O_8$ molecule, and the trivalent aluminium atom replacing the other three. Here the potassium and aluminium atoms, having different valencies, necessarily play different *rôles* in the crystal-structure of the orthoclase, and are present always in the definite proportions represented by the formula $KAlSi_3O_8$. But in other cases we may find two metals of the same valency in a mineral, their atoms sharing a single *rôle* in the crystal-structure, and in such cases a continuous series of mixed crystals is possible. Thus the metasilicates of iron and magnesium, Hypersthene, $FeSiO_3$, and Enstatite, $MgSiO_3$, are isomorphous, and it is possible to get mixed crystals $(Fe,Mg)SiO_3$ containing the two metals in any proportions. Such cases are very common, and consequently very few of the naturally occurring silicates have anything like a constant composition. Not only can one metal replace another, but the atoms of silicon can be replaced partially by those of another tetravalent element, titanium, as in augite, which is shown in the table below.

It would occupy many volumes to describe the silicates in detail. It is only possible here to give a very few examples of the commoner rock-forming silicates, and it will be convenient to arrange them as a series showing the gradual passage from highly siliceous (or acid) minerals to highly basic minerals. The list commences with pure silica, and ends—for the sake of completeness—with an oxide free from silica.

Name of Mineral.	Composition.	Occurrence in Rocks.
Quartz	SiO_2	Occurring in **acid** rocks, such as granite.
Orthoclase Felspar	$KAlSi_3O_8$	
Biotite Mica	$[K,H]_2[Mg,Fe]_2[Al.Fe]_2(SiO_4)_3$	
Augite	$mCa[Mg,Fe](SiO_3)_2+$ $n[Mg,Fe][Al,Fe]_2[Si,Ti]O_6$	Occurring in **intermediate** rocks, such as syenite.
Plagioclase Felspar (variety, Anorthite)	$CaAl_2(SiO_4)_2$	Occurring in **basic** rocks, such as gabbro.
Olivine	$[Mg,Fe]_2SiO_4$	Occurring in **ultrabasic** rocks, such as peridotite.
Magnetite	Fe_3O_4	

The molten silicates are miscible with one another at high temperatures, forming a single uniform liquid or "magma." But, when such a mixture solidifies, the rock formed will consist of a crystalline aggregate of two or more different minerals, unless, of course, cooling is so quick as to cause the formation of a glass. The column on the right of the table indicates some of the rocks in which the different minerals commonly occur.

Consolidation of an Intrusive Mass. We must now consider what will happen when a mass of molten igneous rock is pushed up into the upper, and relatively cooler, portion of the earth's crust. The greater part of the molten rock will probably remain far below the surface, forming a sort of "magma-reservoir," from which will be pushed out fingers through the "country rock"—possibly a limestone, shale or sandstone formed long before the intrusion took place. Wherever one of these fingers reaches the surface, a volcano will be produced. The molten stream which escapes from the crater or fissure soon hardens to a glassy, or semi-glassy rock (lava), the cooling being too quick for complete crystallization to take place. Much of the molten rock forced upwards and outwards from the magma reservoir never reaches the surface, and great sheets of it cool and solidify within the country rock; these sheets, which are often afterwards exposed to view where the country rock has been removed by denudation, are called **sills** where they have been forced between the beds of sediments, and **dykes** where they cut across the beds (see Fig. 18). Sometimes the overlying strata have been pushed upwards at some point as a gigantic blister, allowing the formation of a dome-shaped mass of intrusive rock, which is known as a "**laccolite.**"

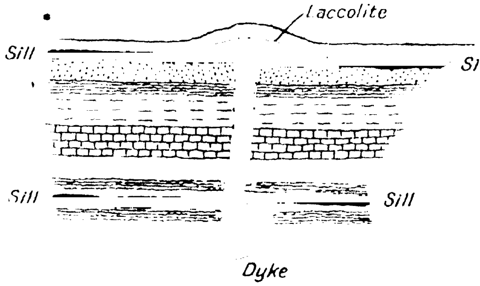

FIG. 18.—Dykes, Sills, and Laccolites.

The solidification of molten rock gives rise to a considerable amount of "**differentiation,**" the composition of the solid rock produced varying from place to place.[1] The ultra-basic minerals, which are not very soluble in the magma, separate first. If the intrusion is a small one, i.e. a dyke, we may expect to find an excess of ultra-basic minerals in the parts which cool first, namely at the extreme edge of the intrusion. Consequently, the margin of such intrusions is usually distinctly more basic than the interior. However, this type of marginal differentiation, although of great interest, is of little importance, except within such intrusions as dykes, where the opposing walls are comparatively close together.

In the interior of any intrusive mass, and especially in large deep-seated magma-reservoirs, segregation of the basic and acidic constituents apparently takes place in a rather different way.[2] As already mentioned, the more basic minerals separate first on cooling, but as a rule they are very much heavier than the acidic portions which still remain liquid, and sink down towards the bottom, or in case there is no bottom, towards the centre of the earth. The portions in the higher parts are thus left relatively acid, and when they solidify on further cooling, form such rocks as granite. Since we naturally have more opportunity of seeing the higher parts of the intrusion than the lower ones, granite is a rock much more commonly met with than the basic crystalline rocks, which are usually produced deep down in the earth. It should be noticed that the lava which is ejected from the volcanoes in the early stage of an intrusion often represents the composition of the magma before this differentiation has taken place, and is therefore of intermediate composition. If lava is spurted out after differentiation has taken place it is of a more acid character (rhyolite) or a more basic character (basalt) according to the place in the magma-reservoir from which it has come.

It is probable that—in addition to the actual settling of the first formed crystals—another factor plays a great part in causing the separation of the acid and basic portions of the magma. If earth-movements such as would tend to force the magma upwards into the crust continue during the process of solidification, they will squeeze out the still molten acidic portion which will rise into the crust, whilst a semi-solid "mush," having on the whole a distinctly basic composition will remain below. It may happen that this basic segregate may afterwards be pushed upwards, possibly into another part of the crust, and may there become completely solid. Consequently, we do find large masses of basic crystalline rocks near the surface, although they are somewhat less common than acid crystalline rocks. Sometimes we find an igneous rock having an acid composition in its main part but containing large streaks of ultra-basic composition ; this suggests that portions of the basic segregate may have become entangled in the stream of lighter acid magma when the latter was being forced upwards into the present position.

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[1] The physical chemistry of the differentiation (fractional crystallization) process in rock magma is well treated by J. H. L. Vogt, *J. Geol.* **29** (1921), 318, 426, 515, 627.

[2] Compare the views of N. L. Bowen, *J. Geol.* **23** (1915), Supplement; **27** (1919), 393; and those of A. Harker, "Natural History of Igneous Rocks" (Methuen).

The existence of ultra-basic rocks is of some importance because certain important ores are found in them. The mineral magnetite (Fe_3O_4) which has some value as a source of iron, as well as the ores of platinum, chromium and—in some cases—nickel, are all found in highly basic rocks, being heavy substances only slightly soluble in a silicate " melt." Platinum and chromium occur only in minute traces in the original magma, and if it were not for the fact that they have become " concentrated " in the ultra-basic rocks, their production on an industrial scale would be almost impossible.

It is, however, the final stages in the consolidation of an igneous intrusion which are of special importance. Suppose, for instance, that the greater portion of an acid intrusion has nearly completely solidified, forming a mass of solid granite, but that in the interior, a certain amount of material still remains liquid. As the solid granite cools, it continues to shrink and no doubt cracks appear in it, and also in the country rock around. The shrinkage forces the still molten liquid from the interior through the cracks in the granite out into the cracks which exist in the country rock. Now this matter which has remained liquid until the last will be more acid than the granite itself, and, when it hardens in the cracks, it will form highly siliceous material, such as pegmatite (consisting of quartz and felspar). Thus we find pegmatite veins and quartz veins cutting through the igneous rock and extending into the country rock around.

Many of the rarer metals which existed only in minute amounts in the original magma, and which therefore do not crystallize out during the main stages of the consolidation, become concentrated in the portions which remain liquid to the end, and these will be found in comparatively large quantities in the pegmatite veins and quartz veins. Thus minerals containing molybdenum, tungsten, thorium, the rare earths and other elements are found in pegmatite and quartz veins in amounts which render extraction profitable, although the same elements are only present in minute quantities in the mass of the intrusion.

Amongst the other minor constituents of the original rock-magma are certain substances such as carbon dioxide, hydrogen sulphide and water, which would normally be gaseous at the temperature in question, but which are kept in solution in the magma by the enormous pressure existing in the deeper parts of the earth. The quantities of these substances in the original magma are only small, but they become concentrated in the last solidifying portions, and when these portions are being squeezed out into the country rock, the dissolved substances are liberated. Gases like carbon dioxide, accordingly, travel upwards through the country rock until they reach the air; other substances which are volatile at these temperatures—mostly compounds of fluorine and boron—are liberated in gaseous form, but—as we shall see—usually become decomposed before they go far. Most important of all, water, heavily charged with silica and other dissolved substances, is forced upwards from the igneous mass through fissures in the country rocks; it deposits part of its burden of dissolved substances on the way, and becomes cooler as it rises. But it usually reaches the surface still quite warm and still containing some dissolved mineral matter, and often gases such as carbon dioxide or hydrogen sulphide. This is the origin of "**thermal springs.**"

Mineral Veins. The dissolved matter carried off by the waters leaving the igneous mass is largely silica, and much quartz is deposited in the fissures up which the water passes, the quartz veins being merely the continuation of those formed by the solidification of the extruded portions of the rock-magna. Various other minerals are also deposited in veins, for instance, calcite, barytes and fluorite. In addition, certain compounds of metals which exist only in traces in the original magma, but which become concentrated in the last-solidified portions, are deposited in the veins by the ascending waters. Some of these are the same as those mentioned as constituents of pegmatite veins, e.g. compounds of tungsten and molybdenum. Others consist of the sulphides of the familiar metals, iron, copper, silver, zinc, and lead. Gold is also found in quartz veins, but in the elementary state. It is necessary to lay emphasis upon the fact that in every case these valuable minerals, when found in veins, are invariably surrounded by large quantities of worthless gangue minerals, such as quartz and fluorite.

In the lower part of the veins, the ores of zinc, lead, copper, and silver commonly consist of the sulphide of these metals; in the upper parts, the subsequent action of the air and moisture has usually converted the sulphides to sulphates, carbonates and sometimes oxides. Often percolating waters of "meteoric" origin (due to rain falling upon the earth's surface) dissolve the original "primary" ores at one point, and then deposit them at other points, where some precipitating agent happens to exist; in this way "secondary" ores are formed. It is not always easy in practice to distinguish between the "primary" ores due to ascending (thermal) waters, and the secondary ores due to descending (meteoric) waters.

Besides leading to the formation of veins, the metalliferous waters also deposit minerals in all sorts of cavities in the country rock, which may become "impregnated" with the metallic ores. The waters often interact chemically with the rock itself, limestone being particularly susceptible to such interaction. Waters containing lead in solution frequently dissolve calcium carbonate ($CaCO_3$), the main constituent of limestone, and deposit galena (PbS) at the very points from which the carbonate has been dissolved. The chemical replacement of one mineral by another through the action of circulating waters is known as "metasomatic replacement."

Pneumatolytic Action. The mineral veins produced by ascending water are found at considerable distances from the intrusive mass itself. Other ores which are found close to, or within, the intrusion seem to owe their origin to vapours given off during the last stage of consolidation. Amongst the volatile substances evolved, the compounds of boron and fluorine are most important. These vapours are naturally very reactive and attack not only the country rock, but also the portions of the igneous mass which have solidified at an earlier stage. The main ores of tin have been produced by "pneumatolytic" action of this kind. Tin has a volatile fluoride (SnF_4), which appears to have been given off freely during the last stage of the solidification of certain acid intrusions. By reaction of tin fluoride with water, or with the granite through which it has to pass, **cassiterite** (SnO_2) is formed. This mineral is found in veins and often, to a very important extent, within the granite itself, which has become converted near to the tin-veins to a rock called greissen. Cassiterite is nearly always accompanied by minerals containing boron or fluorine. Other minerals which occur closely associated with boron and fluorine minerals, and which have clearly been formed, at least in part by the agency of vapour, include compounds of lithium, beryllium, and the rare earths.

Contact Changes. Important minerals occasionally occur at the junction of the igneous mass and the country rock, which near the edge of the intrusive mass is so much changed by heat and pressure as to be almost unrecognizable. The main effect of the "metamorphism" is to recrystallize the whole. Limestone is often baked to "crystalline limestone" or marble. The "sills" and "dykes" thrust out into the country rock cause metamorphism at a considerable distance from the main mass of igneous intrusion. In addition to the mere recrystallization of the country rock, chemical interaction with the igneous matter itself sometimes occurs. For instance, it appears that, by interaction between a limestone and an igneous magma, the magma absorbs lime and becomes relatively weak in silica. On differentiation this may give rise to "sub-silicic" rocks containing minerals which do not occur in ordinary igneous rocks. Thus the heavier portions may contain the mineral corundum (Al_2O_3), whilst the lighter portions may contain such minerals as nepheline, rich in alkali metals and poor in silica.[1]

In cases where ore minerals are found at the junction of igneous and sedimentary rocks, or in the altered portion of the sedimentary rock surrounding the intrusion, the ores are generally referred to as "**contact deposits.**" They are most commonly produced where important intrusions cut limestone, a rock which is peculiarly susceptible to alteration. It is unlikely that all contact deposits are formed in the same way. Many are probably due to the action of vapours or magmatic water given off by the igneous mass upon the sedimentary rocks; others may be due to recrystallization or dehydration through heat of minerals previously existing in the sedimentary rock; other so-called contact deposits may really be marginal segregations resulting from the differentiation of the igneous intrusion. Among the best known contact deposits of the world we may mention two; firstly, the "specular" iron oxide of Elba, which occurs in limestone cut by granite and other eruptive rocks; secondly, the copper sulphide ores of the Clifton-Morenci district, Arizona, found in the altered "aureole" caused by the intrusion of quartz-monzonite into limestone. Many writers include the famous lead-zinc-silver ores of Broken Hill, Australia, and the copper sulphide ores of Huelva, Spain, within the term "contact deposits." Since, however, there is no sharp distinction between "contact deposits" and ores formed by pneumatolytic or hydrothermal action, it is not surprising to find that ores which are classed by some geologists as due to contact action are assigned a different mode of origin by other writers.

The Relative Age of the different Accessible Ores. Several times in the geological history of the world have immense earth-movements, accompanied by intrusion, taken place; each of these events has caused some valuable series of ores. The most recent of these upheavals took place in the tertiary age, and caused the formation of the main mountain ranges, such as the Alps and Himalayas, which exist in the world to-day. Although already the forces of denudation have begun to reduce the original height of these comparatively modern mountains, yet the denudation is in the early stages and consequently only the ores of metals which are produced by thermal waters comparatively near the surface are met with in connection with the earth-movements of tertiary times. The ores of mercury, for instance, which are deposited quite close to the earth's surface, are at present met with almost only in the areas affected by these tertiary mountain-building movements, although the actual rocks in which they are deposited are in general much older; no doubt, mercury ores were produced in connection with the earth-movements which occurred earlier in the history of the earth, but these have been removed by denudation. On the other hand, those ores which are produced deep down in the crust close to the intrusive mass itself, are mainly associated with early systems of earth-folding. Those ores of tin which are of the greatest economic importance to-day, are connected with earth-movements of the Hercynian (post-carboniferous) system; no doubt, ores of tin may occur deep down in the areas affected by more recent movement (e.g. in the Alps), but the forces of denudation have not yet caused these ores to become exposed to view, or even rendered them accessible to the miner.[1]

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[1] For this explanation of the origin of the "alkaline rocks," see R. A. Daly, "Igneous Rocks and their Origin" (McGraw-Hill). Also R. A. Daly, *J. Geol.* **26** (1918), 97.

In general, the occurrence of ores is only to be expected in areas which have been affected by important earth-movements, and their distribution throughout the countries of the world is curiously uneven. The series of rich ores of gold, silver, copper, zinc, lead, tin, tungsten, antimony, mercury, and other metals which are found in a circle around the Pacific, occurring in Chili, Peru, Mexico, Sierra Nevada, the Rocky Mountains, Alaska, Japan, the Malay States, and Australia, and differing considerably in age amongst themselves, owe their origin to the earth-movements which have recurred from time to time in this area. The most recent of these movements has produced the ring of giant mountain ranges which encircle the Pacific, and has caused the vast outpourings of lava from numerous volcanoes; in many parts of the Pacific circle (for instance in the Andes) the volcanoes are still active. But the important after-effect of the various earth-movements and intrusions which have occurred at different times has been the production of the ores just mentioned. A rough map is given on page 117 which serves to show the places around the Pacific where rich ores are found.

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[1] J. W. Gregory, *Trans. Chem. Soc.* **121** (1922), 750.

Geo-chemical Classification of Metals. Before leaving the subject of intrusive masses it is convenient to classify the metals according to their place in the magmatic differentiation :—

(1) Metals found in **ultra-basic rocks** and in the ultra-basic portions of intrusive masses in which differentiation has occurred. Chromium, platinum metals, and probably nickel.

(2) **Common** Metals found in the **body** of the intrusive mass (in order, those occurring in the more basic portions being shown first). Iron, magnesium, aluminium, calcium, sodium, potassium.

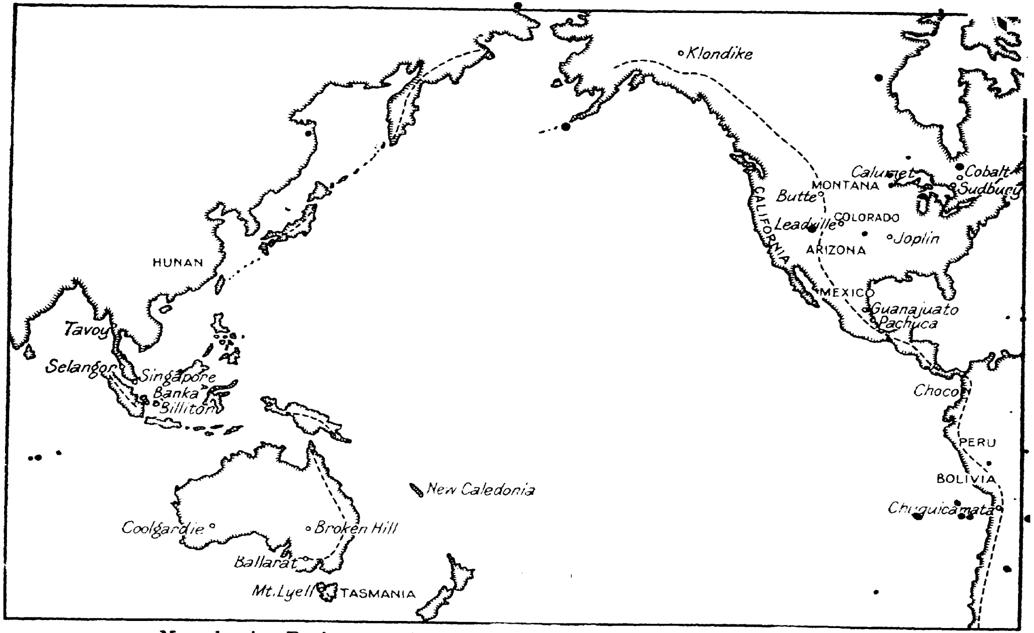
(3) Metals found in the **ultra-acid secretion** in pegmatite veins, etc., either cutting the intrusion or in country rock around it ; or produced by pneumatolytic action (then accompanied by boron and fluorine minerals). Tin, zirconium, thorium, cerium, rare earths, lithium, beryllium, niobium, tantalum, molybdenum, tungsten, uranium, and gold.

(4) Metals found in **mineral veins**, or replacement deposits produced by thermal waters usually some way above the intrusive mass (the lowest are shown first). Copper, silver, lead, zinc, mercury.

Sedimentary Rocks. It is now possible to consider very briefly the mode of formation of different sedimentary rocks. The material carried by the rivers into the sea was in the early days of the earth's history derived from the original crust ; as a result, the original crust quickly became eaten away, and at the present day, there is—according to most geologists—nothing remaining of it. Consequently, all the materials carried away by our modern rivers must be derived from intrusive crystalline rocks, or glassy volcanic rocks, or from sedimentary rocks laid down at some earlier period.

Consider the action of water, in the presence of carbon dioxide and possibly organic acids, on a *crystalline* rock such as granite or gabbro, consisting of silicates and perhaps free silica. The more attackable silicate minerals are likely to suffer a slow chemical change yielding soluble salts, which will be removed in solution by the water ; the eating away of these minerals is likely to cause the rock-mass to soften and break up, and the other—less changed—constituents are liable to be carried off by the water in mechanical suspension.

The silicates rich in sodium, potassium, calcium and magnesium will probably give rise to carbonates or bicarbonates of these metals, which will pass down to the sea in solution. On the other hand, free silica is comparatively unattacked and passes down, in mechanical suspension, as "sand particles." The silicate of aluminium is to some extent attacked by the water, but is converted mainly



Map showing Regions round the Pacific Ocean where Rich Ores are found.

into insoluble hydrated oxides or silicates; sometimes these are left behind where at the position of the crystalline rock as deposits of bauxite, laterite, or similar material; generally, however, most of the silicate minerals rich in aluminium are removed—in a more or less altered condition—as fine "clay particles," which are carried down in mechanical suspension by the rivers to the sea. The silicates of iron are also to a considerable extent attacked by water, especially if organic acids, derived from peat or some other source, are present. The ferrous salts of the acids in question are soluble, but in the presence of air they are oxidized and ferric oxide is thrown down. Sometimes this change occurs at the origin, the "weathered" rocks being stained red or brown with iron; in other cases, most of the iron is carried off into the rivers and often much of it reaches the sea, where ferric oxide is mainly deposited along with the other suspended matter. Ferruginous sandstones have, no doubt, in many cases been formed in this way; if the iron content is high, they may constitute siliceous ores of iron. If, however, the river passes through a lake on the way to the sea, hydrated ferric oxide is likely to be dropped in the comparatively still waters of the lake; the well-known deposits of "Lake Iron Ore" originate in this way.

In cases where a *sedimentary* rock comes under the influence of the forces of denudation, the nature of the process naturally depends on the character of the rock. Limestone is attacked chemically by water containing carbon dioxide, being carried away in solution as a soluble bicarbonate. Sandstone and shale, on the other hand, are mechanically disintegrated, and the resulting particles are borne away in suspension.

A certain amount of suspended matter may be dropped by the river before the water reaches the sea, as for instance where the speed of the water suddenly diminishes. Such river-deposits have occasionally a considerable importance, because if the products of erosion of a crystalline rock should contain grains of the precious metals, such as gold or platinum, these heavy grains will be among the first to sink. The well-known rich **placer deposits** of gold or platinum always occur in the valleys of streams which rise among rocks containing the metals in question. Even when the parent rock contains so little of the precious element that it would not be profitable to crush it, the placer deposits formed are often of extreme value. Heavy minerals containing tin are also found in river-deposits of a similar character.

When the river reaches the sea, the velocity of the water decreases quickly, and the whole of the suspended matter is dropped. Naturally, the coarser silica settles most quickly, being deposited close to the shore as sand, which, if subsequently the sea-bed is raised to form fresh land, will become consolidated into **sandstone.** The finer silicates are carried farther out to sea and there sink to the bottom, forming a deposit, which will finally become **clay, shale,** or—if very high pressure comes to be applied to it—**slate.**

The calcium, magnesium, potassium and sodium salts which are carried down to the sea in solution, are, of course, not deposited on the sea-bottom. Various marine creatures, however, build their hard parts out of calcium carbonate, and in that way most of the calcium is removed from the sea almost as quickly as it is supplied. It is from the hard parts of such creatures—coral, calcareous sponges, foraminifera and various shells-fish—that the important rock known as **limestone** is formed. By the interaction of calcium carbonate—either at the time of the formation of the limestone, or afterwards—with soluble ferrous salts, a great deal of ferrous carbonate may be formed in limestone; such beds may constitute valuable ores of iron.

The remaining soluble salts continue to accumulate indefinitely in the sea. From time to time, however, it happens that a portion of the sea gets cut off from the rest and commences to evaporate. When this occurs, the water will finally become supersaturated with regard to the dissolved salts, which one by one will be precipitated as crystalline crusts. Salt deposits are still in the course of formation in the Dead Sea Valley. Many of the important deposits of soluble crystalline salts which are mined in different parts of the world occur in rocks of the "Permian" and "Triassic" ages, rocks which are known—from independent evidence—to have been formed under dry, desert conditions; for the red sandstone of the same age consists of grains having a form quite unlike that of water-borne sand, being of a rounded form, as indeed is always the case with the wind-blown sand of desert regions. The salt deposits of Cheshire are of this age. Beds of soluble magnesium salts also occur in the Triassic formation.

Amongst the most important deposits of soluble salts occurring in the Permian and Triassic systems are those of Stassfurt (Germany). Besides rock salt ($NaCl$), Kieserite ($MgSO_4.H_2O$), and Anhydrite ($CaSO_4$), we find here beds of Carnallite ($KCl.MgCl_2.6H_2O$), which constitute one of the main sources of the world's supply of potassium.

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When the river reaches the sea, the velocity of the water decreases quickly, and the whole of the suspended matter is dropped. Naturally, the coarser silica settles most quickly, being deposited close passing downwards between them must necessarily become ground. Among the commonest forms of plant for grinding to fine powder, however, are the "**ball mills**" and "**tube mills,**" of which there are innumerable forms; the mill consists in nearly all cases of a cylinder of iron or steel which is mounted with its axis horizontal, and which is kept revolving about this axis. The material to be ground is placed in the cylinder, along with a number of steel balls or flint pebbles which serve to crush the material as the cylinder rotates.

Sizing. No form of crushing or grinding, however, gives a material of uniform size, and, since the fine material will call for a method of metallurgical treatment essentially different from that suitable for the coarse material, the mixture must periodically be passed through some form of sieve or screen having openings of appropriate size, which will serve to separate the coarse from the fine particles. A shaking motion is often imparted to the screen by means of machinery, so as to encourage the smaller particles to fall through the holes. Rotary sieves, known as "trommels," are very useful; they are usually of cylindrical form, and are mounted so as to revolve continuously about a nearly horizontal axis.

For the sizing of the finer portions of ground ores, the rate of sinking of the particles in water is utilized. If the finely ground ore is stirred with water in a tank, and allowed to stand, the comparatively coarse particles or "sands" will soon sink to the bottom, whilst the majority of the very small particles will remain for some time in suspension, as "slimes." The separation into sands and slimes is, however, not entirely a question of size; the sinking velocity of a particle depends not only on the size, but also on the specific gravity; and, since the valuable ore minerals have usually a higher specific gravity than the gangue-material, an ore particle of an intermediate size may enter the sands where a gangue-particle of the same size would enter the slimes. Thus the methods of "classification" into sands and slimes based on the velocity of settling is not purely a sizing process, and may in some ores bring about a certain amount of "concentration." Continuous methods of classification of ground ore into sands and slimes are largely used. One of these is described in the section on copper (Vol. IV).

Concentration. After the crushing and the separation of the coarse, medium and fine portions, it is possible to proceed to the "concentration" proper of each of these portions.

Any process which aims at the separation of two substances, must be based upon some definite difference of properties. The partial separation of gangue or rocky material from the metallic compounds, which we call concentration, usually depends on the fact that the valuable minerals differ from the gangue either in :---

(1) appearance (hand picking processes),
(2) specific gravity (gravity separation processes),
(3) adhesive force, connected with differences in interfacial energy (flotation processes),
(4) magnetic properties (magnetic separation processes),
or (5) melting-point (liquation processes).

The concentration-processes depending on these five differences in properties will be indicated in turn :—

(1) **Hand Picking.** A number of men or women are employed to pick out from a heap of coarsely crushed material those pieces of ore which appear to be rich in precious minerals; they rely mainly on the general *appearance* of the pieces. Obviously such a separation is laborious, and, as a rule, far from complete.

(2) **Gravity Separation** [1] has long been used for the concentration of gold, which is a far heavier substance than the siliceous matter with which it is associated. When the early Californian gold-digger, taking a quantity of gold-bearing sand and water in his pan, swirled out the light sand, whilst retaining the heavy particles of gold in the vessel, he was making use of the difference in gravity. And the somewhat more elaborate system of sluice-boxes, which were installed later in the same region, merely represents a more efficient method of utilizing the same principle.

Gravity separation is of great importance in the concentration of the ores of copper, tin, lead and zinc, and indeed of most other heavy metals. The form of plant used varies according to the size of the crushed ore to be treated.

For particles above $\frac{1}{50}$ inch in diameter, a **jig** is usually employed (Fig. 19). This is a rectangular vessel divided into two compartments which communicate with one another at the bottom. It is filled with water, and in one compartment, a plunger A moves up and down, thus alternately lowering and raising the level of the water in the second compartment. This second compartment is provided with a horizontal sieve B, upon which is placed a "bed" consisting of coarse pieces of rock. The suspension of crushed ore and water is allowed to flow continuously into this compartment at C, above the bed, and the lighter (worthless) constituents, which are kept in suspension by the "up and down" motion of the water, are drawn off continuously with the overflow, D, at the other end. The heavy and valuable constituents sink in spite of the motion of the water, and are either drawn off through a discharge opening (E) arranged at a low level (i.e. just above the bed) or—in another form of jig—pass down through the sieve, being drawn off below.

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[1] See R. H. Richards, "Ore Dressing" (published by the *Engineering and Mining Journal*).

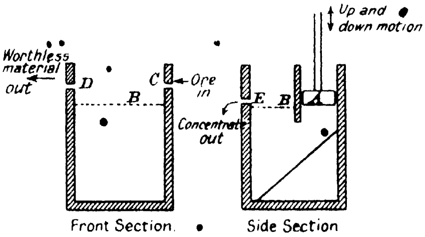

FIG. 19.—Principle of the Jig.

For rather less coarse material ("sands") the **Wilfley table,** or some other form of shaking table, is employed. The Wilfley table (Fig. 20) has a flat surface, covered by thin strips of wood, or riffles, arranged lengthwise. It is set at a slight inclination, the side AB being the higher; mechanism is also provided which imparts a jerking motion to the table, raising the end BC. The pulp of ore and water is introduced from E and tends to flow over the table, and out over the low end CD. The heavier (and more

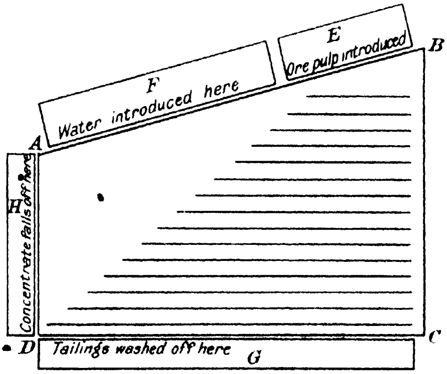

FIG. 20. The Principle of the Wilfley Table (Plan).

valuable) particles, however, get caught behind the riffles, and are gradually made to work along behind the riffles by the jerking imparted to the table, until they are discharged into the trough H, whilst the lighter particles are washed over the riffles by water introduced at F, and pass out separately along the lower end into G.

For still finer material ("slimes") a shaking table would fail to retain even the heaviest particles, and a **vanner** is preferably employed. A typical vanner (Fig. 21) consists of an endless rubber belt moving over rollers, and arranged on a slight incline so that on the upper side, it is continually travelling upwards. The pulp of ore and water is fed on to the belt at A. The heavier material at once sinks and comes into good contact with the rubber; it is consequently carried upwards by the motion of the belt, and is removed at the upper end B. The lighter particles remain suspended, however, and are washed downwards by the water which overflows at the bottom of the belt—or, in another form of vanner, over the side. The whole system of belt and rollers is mounted in such a way that it is shaken mechanically during the operation; the shaking serves to keep the lighter particles in suspension.

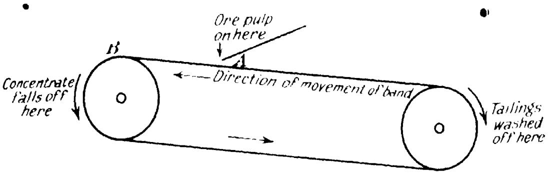

FIG. 21.—Principle of the Vanner.

(3) **Flotation.**[1] This is a most useful process for the concentration of the ores of lead, zinc, and copper, and indeed for sulphide ores generally. It depends on the fact that the sulphides of the heavy metals show a different "adhesive force" towards certain liquids from that shown by the accompanying rock-material. There are numerous variations of the process, but usually the ore is brought into a finely-divided state and made into a pulp with water; small quantities of certain oils are added and the whole is mixed together under such conditions that bubbles of air are introduced into the mixture, yielding a "froth" or "foam." The production of the air bubbles is effected in different ways in different flotation plants. In the "**Mineral separations**" plant, the mixture is churned

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[1] T. J. Hoover, "Concentrating Ores by Flotation" (published by the *Mining Magazine*).

up with rapidly rotating paddles so that air is sucked in by vortex-action. In the **Callow** plant, air is forced into the mixture under pressure by means of a blower, through the porous bottom of the tank in which the pulp is contained. In the **Elmore** process the mixture is sucked up into an evacuated chamber, so that the air which was previously dissolved in the water appears as bubbles owing to the reduction of pressure.

The oil added forms a thin intermediate film separating the air bubbles from the water. If the oil has been suitably chosen, it will be found that the valuable sulphide minerals remain supported, clinging to the thin films which form the walls of the bubbles or foam-cells, whilst most of the worthless silicates sink to the bottom. Thus, if the foam or froth is separated from the comparatively clear liquid below, a very considerable degree of concentration will be brought about.

The success of the process depends mainly on the suitable choice of the oils; the addition must be adjusted so that as far as possible all the valuable sulphides cling to the foam whilst the gangue particles are not attracted. The substances added are usually classified as

(*a*) *Frothers*, such as pine oil, which favour the production of the froth;

and (*b*) *Collectors*, such as coal tar, which favour the adhesion of the minerals to the froth.

Some forms of crude pine tar contain sufficient of both classes. It is generally assumed that a thin film of oil must be formed around the sulphide particles before they can attach themselves to the oil-films surrounding the bubbles of the froth. In certain cases, acid is added to the water used in flotation, a factor which appears generally to favour adhesion of the sulphides to the froth.

The **theory of flotation** is now fairly well understood.[1] It can easily be shown[2] that if two immiscible liquids, A and B, are shaken up with a powdery substance X, and are afterwards allowed to separate into two layers, then

(i) if $\sigma_{BX} > \sigma_{AX} + \sigma_{AB}$, the powder will collect in the liquid A;

(ii) if $\sigma_{AX} > \sigma_{BX} + \sigma_{AB}$, the powder will collect in the liquid B;

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[1] F. G. Moses, *Eng. Min. J.* **14** (1921), 7. A slightly different standpoint is adopted by I. Langmuir, *Trans. Faraday Soc.* **15** (1920), iii, 62.

[2] W. Reinders, *Koll. Zeitsch.* **13** (1913), 235. Compare F. B. Hofmann, *Zeitsch. Phys. Chem.* **83** (1913), 385.

and (iii) if $\sigma_{AB} > \sigma_{AX} + \sigma_{BX}$, or again, if no one of the three values σ_{AB}, σ_{AX} and σ_{BX} is greater than the sum of the other two, the powder will collect at the interface of A and B.

(σ represents the interfacial energy between the two substances suffixed).

In commercial flotation practice, A represents the watery phase (containing the water-soluble constituents of the oils added), B represents the oily phase, which is itself distributed in thin films around the air-bubbles. The additions of oil and, if necessary, acid must be so adjusted that, when X represents a worthless silicate particle, condition (i) holds good, but when X represents a valuable sulphide particle, either condition (ii) or condition (iii) holds good. In this adjustment, those constituents of the crude oils which dissolve in the water, and which alter the values of the interfacial tension between the water and the mineral, probably play as important a part as the oily constituents proper.

Of course in practice the conditions which make for successful flotation have been arrived at empirically, as the result of experience, and not been calculated from the values of interfacial tension, which, in many cases, has never been measured.

(4) **Magnetic Separation.**[1] Many minerals differ greatly in magnetic properties from the rocky substances which occur with them. The most magnetic mineral found in nature is magnetite, but many other iron minerals become converted in part to magnetite, and thus acquire highly magnetic properties, if the crude ore is roasted. Magnetic methods have been used for concentrating certain iron ores, but they are used much more for freeing tin-ores from certain minerals like wolfram and copper pyrites, which are either magnetic or become magnetic on roasting.

Many forms of magnetic separators have been devised, more than one type being designed by Wetherill. In one of the best-known types (shown diagrammatically in Fig. 22) the finely crushed ore is charged at H on to an endless travelling belt, A, which conveys it below the north pole of an electro-magnet M_1; the magnet raises the more magnetic particles from the first belt, and brings them into contact with the lower side of a second belt, B, travelling at right-angles. This belt moves them away to the side, and, when they get out of range of the magnetic field, the particles drop off into a recepticle. Often a second and more powerful magnet

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[1] G. G. Gunther, "Electro-magnetic Ore Separation" (Hill Publishing Co.).

M_2, provided with a second belt C, is installed to lift and remove those feebly magnetic particles which are not lifted by M_1.

(5) **Liquation.** Sometimes the valuable mineral is considerably more fusible than the gangue, or vice versa. Stibnite (Sb_2S_3), the commonest ore of antimony, is much more easily melted than the substances with which it is associated. If, therefore, the product from the mine is heated in a series of pots having holes in their bottoms, the stibnite melts and runs out through the holes, leaving the worthless material behind. Considerable concentration is thus brought about, but the process is wasteful.

The separation of valuable from valueless material by any of the above-mentioned processes is, of course, far from complete, even if the process be repeated several times. They serve, however, to bring up the content of the metal to a value which makes it possible for the metallurgy proper to commence. Some ores—notably those of iron—are rich enough to pass to the smelter without preliminary concentration.

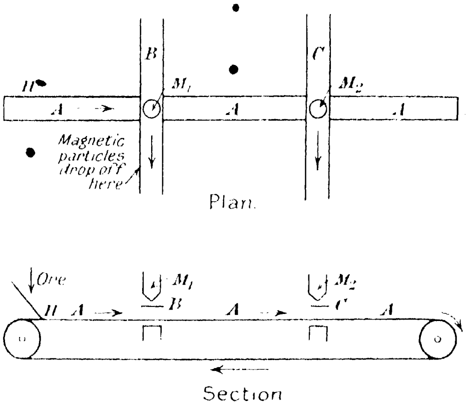

FIG. 22.—Principle of the Magnetic Separator.

Metallurgical Operations. **Metallurgy** may be described as the technical preparation of metals in the elemental condition. It has already been stated that the majority of metals occur as sulphides. In one very common system of metallurgy, the sulphide is first converted to an oxide by **roasting**, that is by heating under such conditions that the oxygen of the air has constant access to the charge. The reaction may be expressed by the following general equation (in which M represents a typical metal):—

$$MS + 3O = MO + SO_2$$

The oxide is then "reduced" to the metallic condition by heating with coal, coke, or carbon monoxide :—

$$MO + C = M + CO$$
$$or\ MO + CO = M + CO_2$$

Where the metal exists in nature as an oxide or carbonate roasting is not necessary, but the ore must nevertheless be "calcined" or strongly heated in order to drive off water and carbon dioxide.

In the case of sulphide ores, an alternative treatment, known as "**roast-reaction,**" is possible. The ore is partly roasted so as to change part of the sulphide to oxide, which is then heated more strongly with unchanged sulphide, so as to yield the metal; the reaction may be expressed thus :—

$$MS + 3O = MO + SO_2$$
$$MS + 2MO = 3M + SO_2$$

Indeed, in certain cases, it is possible to burn off the sulphur from a molten sulphide in a single operation, simply by forcing a blast of air through it, or over the surface. The heat of combustion of the sulphur helps to maintain the temperature, and thus to economize fuel. Even under these circumstances, it is quite likely that the change really takes place in the two stages indicated above; but it can be expressed conveniently by the single simple equation :—

$$MS + O_2 = M + SO_2$$

Slags. Of great importance in any smelting process is the character of the slag obtained. The slag represents, essentially, the rocky constituents of the ore in a molten condition, and consists therefore mainly of a mixture of silicates. At very high temperatures, it is a moderately mobile liquid, but, as the temperature drops, it becomes viscous and pasty, hardening at a still lower range to a glassy or semi-glassy mass. Since silicate mixtures (or slag) are practically immiscible with sulphide mixtures ("matte"), and with molten metals, the slag always forms a separate phase, floating on the top of the matte or metal.

The consistency of the slag at a given temperature depends very much on its composition; if it is too acid or too basic it becomes stiff, and may even "freeze," and block the furnace. In order to obtain a consistency suited for the furnace operation, it is often necessary to add constituents which will alter the character of the slag. For instance, calcium carbonate may be added as a flux to make a highly siliceous slag more basic, and hence more fusible.

In many processes, the slag enters largely into the metallurgical reactions, and in such cases its composition must be carefully maintained within the correct limits. For instance, in the manufacture of steel, it is possible by using a suitable slag to remove most of the phosphorus from the metal. The phosphorus is oxidized, and enters the slag as a phosphate. For this purpose a slag having a distinctly basic character is required, the free basic oxide being needed to combine with the acidic oxide of phosphorus (P_2O_5). A highly siliceous slag is useless for removing phosphorus.

Types of Furnaces. The type of furnace suitable for a metallurgical process depends not merely on the nature of the process, but on the physical character of the raw material. If the ore comes up for treatment in large lumps, the process can often be carried out with advantage in a **blast-furnace** (Fig. 23A). Ore and fuel are fed into the furnace at the top, whilst the air required to burn the fuel is forced in at a considerable pressure at the bottom, and travels upwards through the mass; metal and slag are tapped through two holes below.

A large proportion of the ore, however, comes up for treatment in a rather fine state of division; the majority of the "concentrates" produced by the methods described above are also of a fine character. If more than a small amount of "fines" are included in the blast-furnace charge, the shaft of the furnace will become blocked, or, alternatively, the fines will be blown out of the furnace by the pressure of the blast. In the case of some materials, it is possible to cast the fines into briquettes, or, by sintering, to convert them to nodules, which may be treated like the lump ore.

Generally, however, it is best to treat the finer ores by a different process to the lump ore. In such cases, the **reverberatory furnace** (Fig. 23B) gives better results; it is also used in some cases for lump ore. The fuel is burnt in the "grate" of the furnace, and the flame of hot gas thus produced is deflected downwards by the roof on to the ore-mixture placed on the "hearth." In the more recently designed reverberatory furnaces, we meet with a general tendency for the hearth to become longer and longer; the extra length allows the hot gases to give up a greater proportion of their heat to the charge, and an economy of fuel is effected. Fig. 23C shows a long-hearth furnace. For many purposes, however, the short-hearth furnace is still necessary, especially where the charge has to be kept at a very high temperature.

In many reverberatory furnaces, coal is still employed as the fuel. Those used for steel-making are almost invariably fired with producer-gas, whilst the long reverberatories employed in America for the smelting of copper are often fired by the injection of coal-dust or oil at one end; in such furnaces, the "grate" can be omitted.

If the furnace is required merely for roasting or the calcini
of ores without actual fusion, ground space is saved by replaci
one long hearth by a series of short hearths one above the oth
In the **multiple-hearth** roaster shown in Fig. 23D, the fine o
enters at the centre of the top hearth and is worked towards t

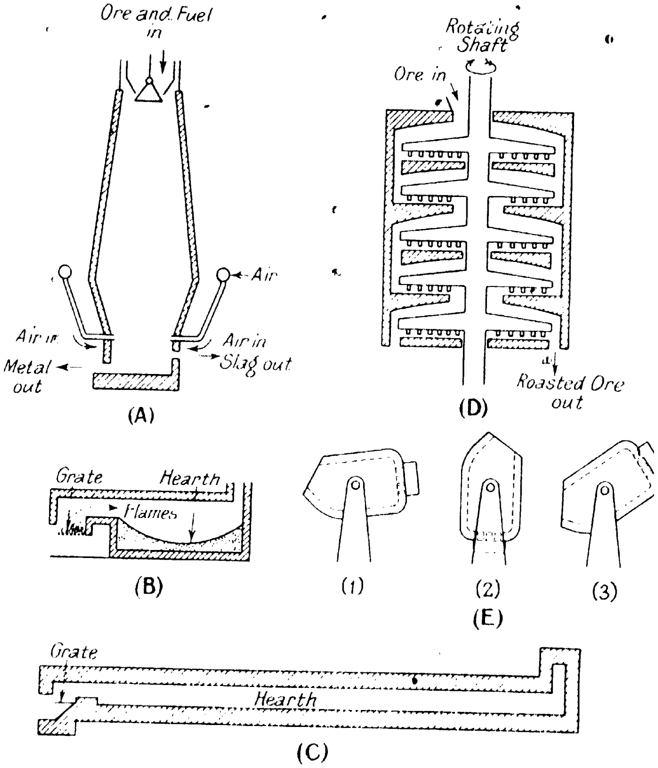

FIG. 23.—Some General Forms of Furnaces.

A) Blast furnace. (B) Short hearth reverberatory furnace. (C) Long hearth reverberatory furnace. (D) Multiple hearth roaster. (E) Converter.

dge by means of rabbles fixed to a rotating arm ; at the edge
t drops to the hearth below where it is rabbled inwards to the
entre. Here it drops to the third hearth, and thus it traverses all
he hearths in turn, finally emerging in a roasted condition from
he lowest hearth. The hot roasting gases are provided by an
utside fireplace and traverse the roaster in the opposite direction.

As the charge is continually being turned over and stirred up by the rabbles, the gases come into effectual contact with all parts of the ore. Where a rich sulphide ore is being roasted, the heat of the oxidation of the sulphur is often sufficient to keep the temperature at the required level; in such a case no outside fireplace is needed.

Special types of furnaces are needed in cases where it is desirable that the charge should not come into direct contact with the heating gases. Such charges may be placed in closed **muffles, retorts** or **crucibles,** round the outside of which play the flames. As it is clearly necessary—owing to the imperfect conductivity of the retort-material—to maintain a higher temperature outside the retort or muffle than is required inside, this form of heating is a wasteful one. For that reason, attempts have been made to raise the temperature of the charge electrically, and so to dispense with heating gases, whilst allowing the heat to be generated in, or close to, the charge itself. "**Electro-thermal processes,**" as they are called, will be described in connection with iron and steel (Vol. III) and zinc (Vol. IV). These processes, which introduce many problems of their own, are most likely to be successful where electrical energy can be raised from water power. Where the electrical energy has to be obtained indirectly from the combustion of coal, by means of an engine and a dynamo, losses of energy necessarily occur.

Another special type of furnace which may be mentioned here is the **converter.** It is used only for those processes in which an easily oxidizable element is "burnt off" by passing air through—or over the surface of—the molten material, the addition of carbonaceous fuel being unnecessary owing to the heat given out by the reaction. The converter is not usually employed for the direct treatment of ores, but is utilized, in two important cases, to work up materials obtained by previous processes. One case is the removal of carbon and silicon from cast iron, in the Bessemer process of steel-making. The other is the removal of iron and sulphur from copper matte (a mixture of copper and iron sulphides) in order to obtain blister-copper.

The converter (Fig. 23E) is usually a pear-shaped vessel, supported at the centre, and is capable of being swung into position (1) for filling. It is then swung into position (2) and air is blown in through tuyeres in the bottom or at the side of the converter until the drooping of the flame shows that the objectionable element is eliminated, after which the converter is tipped into position (3) to pour the finished metal out.

A word must be added about the **lining** of furnaces. In the blast-furnace there is a considerable mechanical wear upon the sides, caused by the rubbing of the descending charge. The fire-brick lining of the blast-furnace used for pig-iron production requires occasional renewal. For the smelting of copper and lead ores, a "water-jacketted" blast-furnace is often employed. Here the structure has two walls of metal one inside the other, the space between the walls being filled with cooling water. As a result, a layer of solidified ore freezes over the interior surface, and constitutes the true lining of the furnace. The wear upon the meta walls in thus greatly reduced.

In other types of furnace the chief factor which causes the lining to wear away is the chemical action of the slag. The material used for the lining must be chosen according to the slag obtained in the process. A basic lining would react with an acid slag; an acid lining with a basic slag. In steel-making in particular, a slag is essential which possesses either marked basic or marked acid properties; if an acid slag is employed then the lining must be acid if a basic slag, then the lining must be basic. Acid linings are usually made of silica in the form of sand, or sandstone; basic linings consist of calcined magnesite or dolomite.

Cold Extraction of Metals. It has already been remarked that the furnace-treatment of "fines" presents many difficulties In such cases it is often worth while to consider whether it would not be more profitable to extract the valuable constituents by "leaching" with an aqueous extractant at a low temperature Leaching may sometimes prove remunerative with low grade ores or tailings which are not worth treating in other ways. The extractants which have been employed are potassium cyanide and sodium cyanide (for gold), sodium chloride, cyanide or thiosulphate (for silver), sulphuric acid (for copper and zinc) and ammonia (for copper). If the metallic compounds contained in the ore are not directly soluble in one of these reagents, the ore is first roasted. The roasting converts sulphides to sulphates and oxides. In the so-called "oxidized ores," which are especially suited for wet treatment, this conversion has already been brought about by the forces of nature. In certain cases, sulphide ores are roasted with sodium chloride, which converts the sulphides to chlorides.

Whether roasted or not, the finely divided ore is treated with one of the extractants mentioned above in a series of "leaching vessels." Assuming that sulphuric acid is the extractant chosen it will act upon the oxide, producing a soluble sulphate, thus:—

$$MO + H_2SO_4 = MSO_4 + H_2O$$

When the solution passes out from the last vessel of the series it is usually taken to electrolytic cells, where an electric current is passed through it, the free metal being deposited upon the cathode and oxygen eliminated at the anode:—

$$MSO_4 + H_2O = M + O + H_2SO_4$$

Since the original extractant—in this case sulphuric acid—is to a considerable extent regenerated, the liquid can generally be used again for the treatment of further quantities of ores. Sometimes, however, the metal is liberated—not by an electric current—but by means of another less valuable metal; in such cases, the solution is usually of no further value, for the extractant is not regenerated. Metallic copper can be liberated from a sulphate solution, for instance, by means of scrap iron, the iron sulphate produced being generally thrown away:—

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

Preparation of Compounds. Besides the elemental metals, there are many metallic compounds which are of technical importance. In the case of easily reducible metals, such as lead, these are commonly prepared from the metal itself. Where the reduction of the metal proceeds with difficulty, as in the case of aluminium or of sodium, the useful compounds are prepared from the natural source of the metal by processes which do not involve an intermediate passage to the metallic condition.

PART I

THE STUDY OF THE METALLIC STATE (METALLOGRAPHY)

CHAPTER I

THE STRUCTURE OF SIMPLE METALS AS THEY SOLIDIFY FROM THE FUSED STATE

It is generally recognized that the structure of metal which has solidified from the molten state is crystalline in character. Since, however, a mass of cast metal differs so strikingly from what is usually regarded as a typical crystal, it is necessary to consider in what sense the word "crystalline" is applied to metals.

When a single crystal of sodium chloride is grown from a supersaturated salt solution, a more or less perfect geometrical form is obtained—usually a cube. If, instead of a single crystal, a large number of smaller crystals are deposited, these will also approximate to the cubic form; but, where two different crystals have grown into contact with one another, the free development is necessarily stopped at the points of contact, and the cubic form of each individual is to that extent modified.

Freedom of growth is evidently a necessary condition for the development of the perfect geometrical form. But the external form is believed to be only the outward sign of the regular arrangement of atoms throughout the whole crystal. Presumably, the ordered arrangement of atoms will persist even when, owing to lack of space, the external form has ceased to be regular. If, for instance, we fuse a quantity of sodium chloride in a vessel and allow it to solidify, the whole mass takes the external form of the vessel. There is, at first sight, no sign of any special geometrical structure, but if the mass is broken up and examined under the miscroscope, evidence may be obtained for regarding the whole as an aggregate of small crystals.

In the same sense, a metal casting is a crystalline aggregate.

Although the external form is merely that of the mould—the casting would be of no use if it were otherwise—the study of a section shows it to be composed of numerous crystal-grains, each of which possesses every property of the crystalline state except that of characteristic geometrical form.

The Preparation of a Micro-section. The preparation of a section is therefore necessary before a study of the structure of a piece of metal is possible. Working details of the process must be sought elsewhere [1]; only a rough sketch of the operation can here be given. The metal is sawn across at the point where the internal structure is to be examined and a specimen about 1 cm. square and about ½ cm. thick is cut out. The face to be examined is then made approximately flat by grinding with a file, or, in cases where this would cause a permanent alteration to the structure, with emery. If the metal is too hard to be sawn, a sledge-hammer must be used to break off a piece, which is then ground flat with emery or carborundum.

Having obtained a comparatively flat surface, it is necessary to continue the **grinding** with French emery paper, using first a comparatively coarse variety, but gradually increasing the fineness of the emery employed until the surface appears to be smooth and brilliant. It is then ready for **polishing,** which is best performed with a wet cloth mounted on a revolving disc. A suitable polishing powder should be used on the cloth, fine alumina or rouge (ferric oxide) being the most satisfactory. "Globe Polish" on "Selvyt" cloth is useful for polishing the softer alloys.

Polishing is an essentially different process from the grinding with emery. The action of the emery is one of cutting, and causes a series of minute parallel grooves upon the surface. The fine emery removes the striations caused through the previous rubbing with coarse emery simply by wearing down, or cutting across, the ridges that separate the grooves. But, however fine the last emery paper to be used may be, a series of striations will always be left, although it may require a microscope to see them. The polishing operation removes these last fine striations by causing material to flow down from the ridges into the grooves, and the whole surface becomes absolutely smooth. The theory of the polishing process, which may be described as a process of "smearing," is dealt with more fully in the next chapter.

The polished section has now to be **etched** in order that the structure may become evident under the microscope. Generally the specimen is simply immersed in a suitable solution; occasionally gentle rubbing during etching may be advisable; in one method—now seldom employed—the operations of polishing and etching are combined. Various corrosive substances are used for etching different metals,[1] as shown below:—

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[1] C. H. Desch, "Metallography," Chap. VII (Longmans, Green & Co.).

For iron and steel: picric acid (alcoholic), nitric acid, cupric ammonium chloride, ammonium persulphate, hydrochloric acid.

For copper and alloys: nitric acid, ferric chloride, ammonia, bromine, ammonium persulphate, cupric ammonium chloride.

For nickel and alloys: ammonium persulphate, ferric chloride, chromic acid, hydrochloric acid.

For tin, lead, antimony, bismuth and alloys: hydrochloric acid, ferric chloride, nitric acid, silver nitrate.

For zinc, cadmium and alloys: sodium hydroxide, iodine, nitric acid, chromic acid, hydrochloric acid.

For aluminium and alloys: sodium hydroxide, hydrofluoric acid, hydrochloric acid.

For gold and platinum: aqua regia (a mixture of nitric and hydrochloric acids).

For silver: nitric acid.

Occasionally it is convenient to etch a section electrolytically, by making it the anode in a suitable solution such as citric acid, ammonium molybdate or sodium chloride, and passing a small current through the solution.[2]

It may here be mentioned that, whilst for simple metals the object of etching is merely to display the internal structure of the metal, for alloys—in which the composition varies at different points of the section—the object may be to produce a different colour upon the different components so as to enable the observer to distinguish between them. If this is desired, the etching agent must be carefully chosen. If a steel containing phosphorus is treated with a solution of copper chloride containing hydrochloric acid and magnesium chloride, the purer portions of the steel become coated with copper, whilst the parts containing phosphorus are comparatively unaffected. The differential colouring of the surface of an alloy is also sometimes carried out by the method of "**heat-tinting**," which although not, strictly speaking, a process of etching, may be referred to at this point.[3] If steel containing phosphorus is heated to 300° C. in air, the surface as a whole becomes reddish-brown, owing to the formation of a thin film of oxide; but the parts richest in phosphorus have a distinctly blue colour. For other purposes, tinting may be carried out by exposure to sulphuretted hydrogen gas, which develops a film of sulphide on certain parts of the metal, or by exposure to bromine vapour.

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[1] O. F. Hudson, *J. Inst. Met.* **13** (1915), 193. J. Czochralski, *Stahl u. Eisen*, **35** (1915), 1129.

[2] F. Adcock, *J. Inst. Met.* **26** (1921), 361.

[3] See also J. Stead, *J. Inst. Met.* **11** (1914), 135.

Examination of a Micro-section. The etched section may now be examined under the microscope. A common form of the apparatus is shown diagrammatically in Fig. 24.[1] Light from the source A is directed by the condenser B, through the adjustable aperture D, and striking the glass plate E is reflected downwards through the lens F, on to the specimen G, which is mounted upon the stage H of the microscope M; in this way the surface to be examined is illuminated by light falling on it vertically—a condition which is generally desired for the study of a section. The lenses F constitute the objective of the microscope, the eyepiece being J. When the observer's eye is placed above J, he sees the illuminated specimen G greatly magnified.

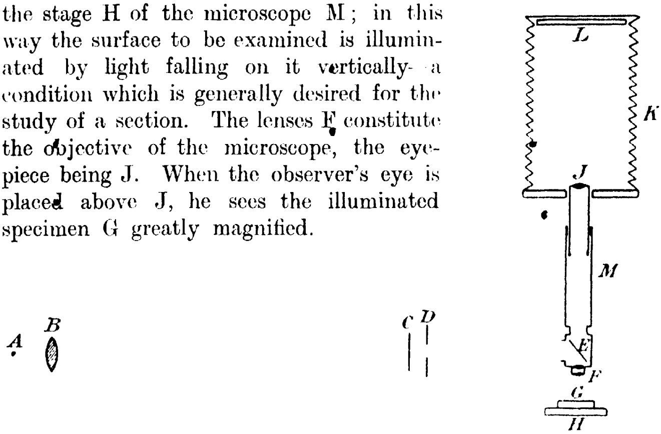

FIG. 24.—The Micro-photography of a Section.

In order to obtain good definition it is essential that the surface under examination should be exactly at right angles to the optic axis of the microscope, and various devices have been introduced to facilitate the adjustment of the specimen in the desired position.[2] It is also generally advisable to introduce a coloured screen in the path of the light, say at C, since even the most carefully corrected lenses do not always bring rays of different wave-lengths to a focus at exactly the same point; a green screen is generally employed.

When it is desired to photograph a section, instead of merely to study its structure, the camera attachment K must be added.

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[1] For further details of metallurgical microscopes, see J. H. G. Monypenny, *Trans. Faraday Soc.* **16** (1920), i. 140. W. Rosenhain, *Trans. Faraday Soc.* **16** (1920), i. 128. L. Aitchison and F. Atkinson, *Trans. Faraday Soc.* **16** (1920), i. 152. C. H. Desch, *Trans. Faraday Soc.* **16** (1920), i. 135. H. M. Sayers, *Trans. Faraday Soc.* **16** (1920), i. 166.

[2] See for instance W. Rosenhain, *J. Inst. Met.* **13** (1915), 160.

which allows the magnified image of the section to fall on to the photographic plate L, which after exposure is developed and printed. For the micro-photography of metallic sections, some workers prefer a horizontal microscope to a vertical instrument.

Appearance of a Micro-section.[1] Fig. A of the frontispiece shows the typical structure of a cast metal. It is a micro-photograph of a section of cadmium which has been etched with a mixture of chromic and nitric acids. The metal will be seen to consist of small polygonal grains, separated from one another by sharp boundary lines which are smooth but in many cases somewhat curved. Other metals show a similar granular structure, although in some cases the boundaries of the grains may be less regular. Fig. C shows the boundaries separating three large grains of lead, whilst Fig. F shows the granular structure of annealed cupro-nickel.

It will be noticed in Fig. A that some of the grains appear light and others dark. This is not due to any real difference between the natural colour of different grains, for if we were to allow the light to strike the surface at a different angle, the grains which now look dark would become light, whilst those which are now light would appear dark.

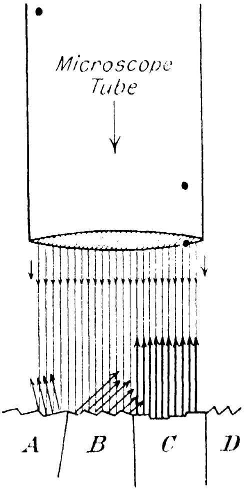

FIG. 25.—Showing why some Grains in a Micro-section appear bright and others dark.

If a section of this kind is carefully examined in a microscope of still higher power, the reason why some grains appear light and others dark becomes evident.[2] It will be found that the action of the etching solution has produced, not a general wear upon the surface, but a series of well-defined parallel facets upon each grain, all of which reflect the light in the same direction (see Fig. 25). The fact that the surface has been corroded more in some directions than in others affords evidence that the atoms in each grain are arrayed in a definite orientation, that is to say, that the grain is crystalline. Since the facets remain parallel throughout one grain, evidently the orientation of atoms is the same throughout the whole of that grain; in other words, each grain represents one crystal.

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[1] See J. A. Ewing, *J. Inst. Met.* 8 (1912), 4.
[2] J. E. Stead, *J. Iron Steel Inst.* 53 (1898), 145, especially pages 174–176.

Where we pass from one grain to another, however, the inclination of the facets to the surface changes. Thus one grain (e.g. grain C) may reflect light up the microscope tube, and appear light, whilst its neighbours reflect light in other directions and so remain dark.

If we consider for a moment the conditions under which the molten metal has solidified, a reason for the granular structure will become apparent. Suppose that a mass of hot molten metal is allowed to cool down slowly and uniformly. As soon as it falls below the melting-point, the metal may be said to be "super-cooled," and is in a condition to crystallize if nuclei are provided. When the temperature has sunk some degrees below the melting-point, the super-cooling is such that nuclei appear spontaneously; that is to say, at various points within the liquid, groups of atoms commence to array themselves in the stable crystal-arrangement, and the minute crystals so produced continue to grow out in all directions. Now, if the cooling has been slow and the temperature is uniform, the nuclei will be distributed fairly uniformly throughout the body of the metal. Supposing, in Fig. 26, that nuclei appear in a mass of metal at the points *a*, *b*, *c*, *d*, *e*, and *f*, and crystallization spreads out in all directions from these points, until the solid metal produced by crystallization from one point meets that produced by crystallization from another. Evidently when the whole metal is solid, the structure will consist of numerous minute grains each of which has grown out from a separate nucleus; and, if the nuclei have been distributed in a fairly uniform manner throughout the mass of metal—which should be the case if the temperature was uniform throughout the mass during cooling—all the grains should be of the same sort of size. But, whereas the rows of atoms constituting the grain A, which has been formed by crystallization spreading from the nucleus *a*, will be orientated in one direction, the atoms of the grain B, which has grown out from the nucleus *b*, will have a quite different orientation. This is shown particularly well by an actual micro-photograph of stressed lead (Fig. C of the frontispiece). The series of parallel dark lines ("slip bands"), the nature of which will be discussed in the next chapter, afford an indication of the direction of the natural rows of atoms in each crystal. It will be noticed that the direction is quite different in each of the three grains shown in the micro-section.

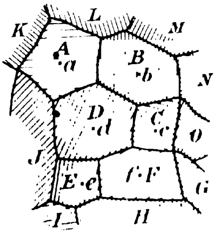

FIG. 26.—Equiaxed Polygonal Structure of a Metal which has crystallized from uniformly distributed Nuclei.

The theory of crystallization from nuclei explains, therefore, very satisfactorily the formation of the granular structure of slowly cooled metals. The theory may be tested by applying it to a case where polygonal structure is not observed. Supposing that liquid metal is allowed to cool quickly in a metallic mould, which readily conducts away the heat. In such a case, the temperature of the mass is never uniform. The outer portion, in contact with the mould, will fall below the melting-point whilst the interior is still many degrees above it. Evidently all the nuclei will be produced at or very near the surface of the mould (Fig. 27 (A)). Growth will commence from the nuclei *a*, *b*, *c*, *d* and *e* in all directions, but in the direction parallel to the surface of the mould, the solid formed by crystallization from *a*, will soon meet with the solid formed by crystallization from *b*, and in this direction growth must soon cease. On the other hand, in the direction perpendicular to the surface, the crystals can extend almost indefinitely without meeting any others. Therefore, in a case of this kind, long thin crystallites will be formed. In fact, ingots of steel, cast from a high temperature, may consist almost entirely of long thin crystals perpendicular to the walls; the crystals extend from either side into the centre of the ingot, and only cease where they meet with similar crystals which have grown out from one of the other walls, or from the bottom of the mould, as shown in Fig. 27 (B).[1] On the other hand, where the steel is poured into the mould at a lower temperature, the interior portions may pass below the melting-point before the whole is solid. Consequently nuclei are formed in the centre of the mass, and the central part of the ingot consists of the ordinary polygonal grains having nearly equal development in all directions ("equiaxed structure"), whilst the outer portions consist of the long thin crystals perpendicular to the surface. This state of affairs is shown in Fig. 27 (C).

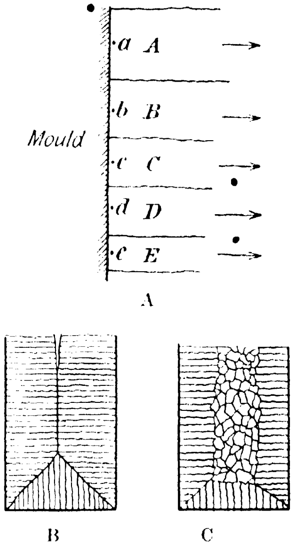

FIG. 27.—Structure produced at the Walls of a Mould.

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[1] A. W. and H. Brearley, *J. Iron Steel Inst.* 94 (1916), 137.

Some idea of the average size of the grains which make up a metal must be given. In metals of high melting-point, cast under conditions which favour the production of an equiaxed structure, the size is often between 0·1 and 0·01 mm. diameter. It is sometimes stated that the quicker a metal is cooled, the smaller the grain-size will be, and this is very generally true. Usually the effect of cooling a metal rapidly below the melting-point is to cause the formation of a very large number of nuclei before there is time for the crystal growing from one nucleus to meet that growing from another; in consequence the grains will have a very small size. But the rule just given is not of universal application because any increase in the degree of super-cooling not only causes an increase in the rate of production of the nuclei, but also affects the velocity of the growth of the crystals extending from those nuclei.[1]

Certain metals of low melting-point, which naturally cool down more slowly in casting than metals whose melting-point is very high, are commonly met with in grains of quite large size; an example is lead, in which crystals having an area of ½ to 4 sq. inches are easy to produce.

Abnormal shapes and sizes always occur close to a cooling surface. The structure of steel ingots with long thin crystals perpendicular to the sides has already been described; here we may meet with crystals many inches long. The beautiful radial structure observed in an ordinary stick of cast zinc, which is visible when the stick is broken across, is an example of the same effect on a smaller scale; the crystals extend from the circumference to the centre of the stick.

The crystallization of metals in thin layers is often favourable for the formation of grains of visible size. If, in a thin layer, the number of nuclei *per unit volume* is the same as in a thick mass, the number *per unit area* will evidently be greatly reduced; the dimensions of the grains produced should therefore be increased. In the thin layer of zinc on the surface of galvanized iron (produced by the old "hot" process) the large grains are extremely conspicuous.

The Form of the Growing Crystals. The boundary separating two polygonal grains represents, of course, the surface along which the crystals growing from two different centres have met. The form of the grains produced is said to be **allotriomorphic,** being determined by the mutual interference of the different crystals, and it affords absolutely no indication of the shape possessed by the small crystals during their free growth before they meet one another. The granular outline may often happen to approximate to that of a regular square or hexagon, but this must not be looked upon as in any way connected with the well-known geometrical forms shown, for instance, by freely-growing crystals of a salt, nor is the shape of the grains any sign of the crystal-system to which the metal belongs. As a matter of fact, if the growth from the various nuclei had taken place with equal velocity in all directions (the freely-growing crystals being thus a series of constantly expanding spheres), the grains produced when the crystallization was complete would have had the forms of polygons bounded by absolutely straight edges.[1]

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[1] See G. Tammann, "Lehrbuch der Metallographie" (Voss), 1914 edition, pages 16, 17.

Two kinds of observation, however, afford information of the shape assumed by the crystal during its growth. The first concerns the patterns produced upon the free upper surface of a solidifying mass of metal.[2] When molten metal is cooling, it contracts, although in certain metals (e.g. antimony and bismuth) the actual process of solidification is accompanied by an expansion. If crystallization commences at the free surface of a metal, the growing crystallites appear in relief at the surface, whilst the portion which is still liquid continues to recede. When the whole has become solid, we still see a pattern in slight relief upon the surface, representing the shape of the early-formed crystals. Thus we are able to study at leisure the shape assumed by the crystals during the early stages of growth. This study makes it apparent that crystallization from the centres has not spread out in simple geometrical forms, such as cubes or octahedra, but that curious branched skeleton-crystals have been produced. Often the skeleton-crystals have a peculiar resemblance to the forms of plants and trees, and are spoken of as "**dendritic growths.**" Those that cover the surface of aluminium are sometimes fern-like, whilst at other times they recall the appearance of a lettuce-leaf. The crystal-skeletons of cadmium (a metal which crystallizes in the hexagonal system) have commonly the form of a six-rayed star, and a particularly perfect specimen is shown in Fig. B of the frontispiece, a micro-photograph of part of the surface of a cadmium ingot. Dendritic markings are especially conspicuous on the surface of pure antimony, and are known as the "star of antimony."

If we grind away the surface layer, and then polish and etch the metal just below it, we find the ordinary granular structure. There is no sign of fern-pattern, lettuce-leaves or stars within the etched metal; the contrast between Figs. A and B of the frontispiece, which represent respectively the section and the surface of the same metal; cadmium, is very striking. Presumably when the dendritic growths from the different centres in the interior of the metal meet one another, and can grow outwards no more, the liquid crystallizes between the fronds, connecting them together, and destroying all traces of the original dendritic shape. At the surface, this "filling-in" process cannot occur, owing to the liquid portion having receded downwards; and here the dendritic pattern will survive.

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[1] C. A. F. Benedicks, *J. Inst. Met.* **22** (1919), 264.

[2] W. Campbell, *Metallurgie*, **4** (1907), 801, 825.

In certain cases it is possible to watch the development of a crystal skeleton. If lead (a metal crystallizing in the cubic system) is melted in a flat iron dish and allowed to solidify slowly, a very striking effect is produced.[1] One or more arms shoot out from the place where crystallization starts, gradually spreading over the molten metal. Then at intervals along these arms, others appear at right angles to them, and from these grow a third set parallel to the first; then a fourth set strike out at right angles to the third. This process continues indefinitely, causing the gradual filling in of the space between the earlier arms. The growth of each individual crystal proceeds until arrested by meeting the sides of the dish or, alternatively, another crystal. The outline of the growing crystal is suggested in Fig. 28.

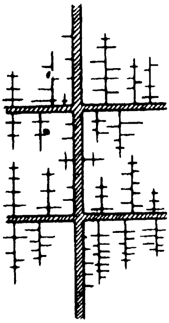

FIG. 28.—Dendritic Growth produced on the Surface of Metal.

Nevertheless, it appears somewhat unwise to draw conclusions as to the events within the interior of a mass from the phenomena at the surface. Fortunately, there is an entirely independent means of knowing that crystalline growth in the interior is of a dendritic character. In the solidification of certain alloys, such as brass, bronze and cupro-nickel, the composition of the first portion to crystallize is often somewhat different from that of the last portion. If a section of such an alloy is treated with a suitable etching agent, it is possible to distinguish the first portion from the last. It is easy then to see that the outline of the first-formed crystals is dendritic, as is shown in Fig. E of the frontispiece, a section of a copper-nickel alloy (cupro-nickel).[2] Had the metal been a simple one, all evidence of the original dendritic structure would have vanished, when the space between the fronds was filled in.

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[1] J. C. W. Humfrey, *Phil. Trans.* **200** [A] (1903), 225.

[2] Compare F. Adcock, *J. Inst. Met.* **26** (1921), 361. See also the examples of "cored" bronzes and brasses given by O. Smalley, *J. Soc. Chem. Ind.* **37** (1918), 191 T.

The fact that the atoms throughout a polygonal grain have one orientation shows that the whole of the dendritic growth that starts from one nucleus is really a single crystal. It may seem strange that so complicated an outline should result from so simple an internal structure. The production of dendritic forms in solidifying metals can, however, be explained in the following way.[1]

Suppose that the first minute crystal produced from the supercooled liquid metal was a perfect cube (Fig. 29A), and imagine it to grow slightly by the solidification of fresh metal upon it; this solidification causes evolution of heat, and will raise the layer of liquid all round the surface of the cube to the melting-point. Crystallization will then stop, and can only continue when a fresh quantity of the supercooled liquid can reach the crystalline surface by "convection" or, alternatively, when the comparatively hot layer just outside the crystal can give up some of its heat by "conduction" to the cooler liquid round about it. Both the processes occur most easily at the corners of the cube, where the solid is surrounded, as it were, on three sides by liquid; therefore, crystallization occurs more readily at the corners than at any other place, as shown in Fig. 29B. As the diagonal axes are elongated, the conditions become even less favourable for crystallization at points other than the corners, and thus the diagonals grow out farther as shown in Fig. 29C and D. In such a way the crystal skeletons are produced.

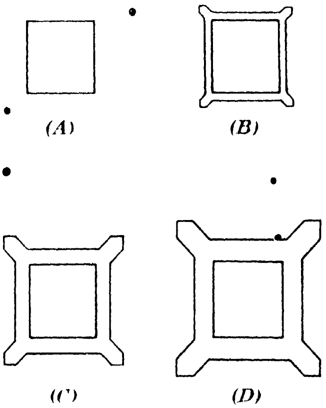

FIG. 29.—Crystal Skeletons produced by accelerated Growth at the corners of a Cube.

It may be mentioned here that dendritic forms are met with under special circumstances, in the crystallization from solution of salts, which normally crystallize in well-marked geometrical shapes. The dendritic habit is commonly obtained when a colloid is added to the solution.[2] The explanation is similar to that given for the appearance of dendritic growth in metals. When a cub crystal of sodium chloride is placed in a supersaturated solutio free from colloids, the natural diffusion will keep the concentration of the solution in contact with the crystal high enough t allow deposition on all parts of the faces; the cubic form i therefore maintained. If, however, a little gum arabic is adde to the solution, the latter becomes viscous and the diffusion i retarded. In consequence, the crystallization occurs more readil at the corners than elsewhere, and a skeleton form is graduall produced.

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[1] R. Vogel, *Zeitsch. Anorg. Chem.* **116** (1921), 21. See also O. Lehmann, "Molekular Physik" (Engelmann), pages 685, 327, 337.

[2] J. H. Bowman, *J. Soc. Chem. Ind.* **25** (1906), 143.

Familiar examples of this fascinating form of crystal growth ar provided by the frost patterns upon our window-panes, and by th shapes observed in snow crystals when they are examined throug a lens.

Determination of the Crystal System in which a Meta crystallizes. It has already been remarked that the shape of th grains observed in a micro-section is no indication of the crysta system to which the metal belongs. The arrangements of the facet produced by etching is, however, a true key to the crystal structure. In the case of some specimens of steel, deep etching produces series of well-marked steps, the corner of each step having the for of the corner of a cube; such a structure would seem to sugges that iron crystallizes in the cubic system. Brittle iron containin phosphorus has actually been broken up along the cleavage plane into perfect cubes. In most cases, more definite information i given by etching of a light character. It is often found that th lightly etched surface is covered with a series of depressions o **etching-pits** bounded by straight faces, and generally having well-marked geometrical form.[2] These etching-pits are occasionally called **negative crystals**; in many cases, they have th form of cubes or octahedra, the general shape of the pits bein similar to the impression left when the side—or perhaps the corne —of a solid cube or octahedron is pushed into soft wax, and is the pulled out again.

Usually the results of etching provide ample evidence regardin the system in which a metal crystallizes. Our conclusions are confirmed by the general character of the dendritic growths produce at the surface of cooling metals. Cadmium, for instance, whic crystallizes in the hexagonal system, often shows a six-rayed sta on the surface (see Fig. B of frontispiece).

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[1] J. E. Stead, *J. Iron Steel Inst.* **53** (1898), 176, with special reference t Plates XVII and XVIII.

[2] J. A. Ewing and W. Rosenhain, *Phil. Trans.* **193** [A] (1900), 357. See also V. Goldschmidt, *Bull. Wisconsin Univ.* (*Science Series*), **3** (1904), 23.

Occasionally, indeed, there is more direct evidence regarding the system of symmetry to which a metal should be assigned. For instance, copper is occasionally found in nature in the form of perfect octahedra, and similar forms have been produced in the laboratory under special conditions; this confirms the view that copper belongs to the cubic system of crystal-symmetry.

In recent years, the X-ray methods of W. H. and W. L. Bragg, Hull and Debye, have made it possible to determine, in many metals, the actual arrangement of the atoms throughout the crystal. Most of the metals have their atoms arranged on a centred cubic lattice or a face-centred cubic lattice, whilst others crystallize in the hexagonal system, as is shown in the table below.[1] Metals belonging to the same group of the Periodic Classification are bracketted together.

Cubic System.		Rhombohedral-Hexagonal System.	Tetragonal System.
Centred-cube Lattice.	**Face-centred Cube Lattice.**		
Lithium	Calcium	Beryllium	Tin ("white")
Sodium	Aluminium	Magnesium	Indium
Titanium	Cobalt	Titanium	
Tantalum	Nickel	Zirconium	
Chromium	Rhodium	Ruthenium	
Molybdenum	Palladium	Osmium	
Tungsten	Iridium	Zinc	
Iron	Platinum	Cadmium	
	Copper	Arsenic	
	Silver	Antimony	
	Gold	Bismuth	
	Lead		

Intra-granular and Inter-granular Fracture. Rosenhain's Theory. If a piece of metal is broken in two, the line of fracture may either pass across the grains, following the cleavage-direction in each grain (**Intra-granular fracture**), or it may pass between the grains (**Inter-granular fracture**). Both types of fracture are known, but the former—at least in the technically useful metals—is much the more common.

This may seem curious. It might seem likely that the boundary where two different grains meet one another would be a "surface of weakness," and that, on the least shock, the two grains would come apart. But that does not appear to be the case; Rosenhain has shown, on the contrary, that, in many cases, the boundar is a surface of especial strength. The theory of an inter-granula "amorphous cement" [1] explains the difficulty adequately, an leads to some interesting conclusions.

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[1] W. H. Bragg, *Phil. Mag.* **28** (1914), 355. L. Vegard, *Phil. Mag.* **31** (1916), 83; **32** (1916), 65. P. Debye, *Phys. Zeitsch.* **18** (1917), 483. P. Scherrer, *Phys. Zeitsch.* **19** (1918), 27. A. W. Hull, *Phys. Rev.* **10** (1917), 661; *Science*, **52** (1920), 227; *Trans. Amer. Inst. Elect. Eng.* **38** (1919), 1445; *J. Franklin Inst.* **193** (1922), 189.

Consider the arrangement of the atoms on the boundary betwee two grains A and B (Fig. 30). The atoms throughout grain A having arrayed themselves under the influence of the crystallizatio from the centre *a*, have one orientation; the atoms throughou grain B, which were arrayed according to the crystallization fro the centre *b*, have another orientation. The atoms at the boundary, however, must come under the influence of crystallization bot from *a* and from *b* simultaneously.[2] It is probable, therefore that the boundary atoms will remain in a more or less disordere state; in other words, when the whole of the metal has cooled t the ordinary temperature, the boundar layers separating the various crystallin grains will have an amorphous characte like that of a glass. As was explained i the introduction (page 46), a glass possesse a structure comparable in some respects t that of a liquid, but must be regarded as liquid so viscous at ordinary temperature as to be absolutely rigid.

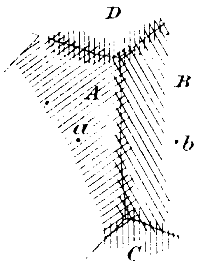

FIG. 30.—Amorphous Layers produced at Grain Boundaries.

In considering, therefore, whether a lin of fracture will pass between the grains o across them, we have to compare th liability to breakage of a glass and a crys tal. As has been pointed out, there ar certain planes in a crystal—the cleavage-planes—along whic fracture occurs with especial ease. A glass, in which the atom are not arrayed on any definite principle, has no cleavag planes and therefore no direction of special weakness. On th other hand, the glass gradually softens as the temperature rises becoming more and more like an ordinary liquid, whereas a crysta retains its strength almost unimpaired up to the melting-point above which the strength suddenly drops. The curves of Fig. 3 show the way in which the strength of the crystalline and amor phous (glassy) forms of the same metal vary with the temperature At high temperatures the crystalline form will be stronger, whils at lower temperatures the amorphous form will be the stronger

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[1] W. Rosenhain and D. Ewen, *J. Inst. Met.* **8** (1912), 149; **10** (1913) 119.

[2] See C. A. F. Benedicks, *J. Inst. Met.* **22** (1919), 103. Compare Sir A Ewing, *Trans. Faraday Soc.* **17** (1921), 61, but note the objection raised b C. H. Desch, *Trans. Faraday Soc.* **17** (1921), 79.

The temperature at which the curves cross one another (that is, the temperature at which both forms are equally strong) is a point of some importance; it has been named by Jeffries the **equi-cohesive temperature.**[1]

Since, below the equi-cohesive temperature, the crystalline form is the weaker, the fracture will pass across the grains, as has been observed above; the amorphous phase may at such ranges be regarded as a strong cement, binding the grains together. But, above the equi-cohesive temperature, the amorphous phase will be the weaker, being indeed nothing but a viscous liquid, and the grains should part one from another when force is applied. This has been confirmed by observation. It is found that the fractures of iron,[2] lead,[3] tin,[3] aluminium,[3] bismuth,[3] and copper [4] are generally inter-crystalline at high temperatures, and generally intra-crystalline at low temperatures.

It should be pointed out that the cohesion of the amorphous form of metal at low temperatures is not the only cause of the special strength of the inter-crystalline surfaces. It is clear that, in many cases, there is actual interlocking at the boundary between the dendritic growths which have advanced from either side, and this sort of dovetailing between the grains must add materially to the strength. Nevertheless the special strength of the inter-granular surface appears to exist even where the boundaries of the grains are perfectly smooth, and where no interlocking can be detected in a micro-section. This can only be explained satisfactorily by admitting the existence of the inter-granular amorphous cement.

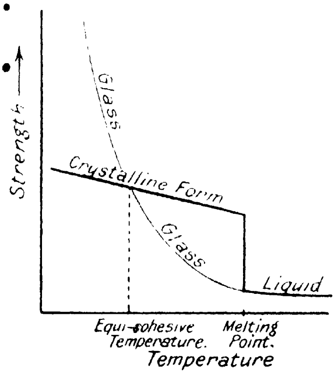

FIG. 31.—Variation of the Strength of the Crystalline and Glassy Forms of Matter with the Temperature.

Inter-granular fracture may occur even at low temperatures if the metal contains an undesirable impurity. If copper contains a small quantity of bismuth, the impurity collects at the boundaries of the different grains, preventing them from meeting each other. Bismuth being a fragile metal, the whole metal is made brittle, the line of fracture being of course inter-granular.[1]

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[1] Z. Jeffries, *J. Amer. Inst. Met.* **11** (1917–18), 300; *Trans. Amer. Inst. Min. Eng.* **60** (1919), 474, especially pages 501 and 502.

[2] W. Rosenhain and J. C. W. Humfrey, *J. Iron Steel Inst.* **87** (1913), 219.

[3] W. Rosenhain and D. Ewen, *J. Inst. Met.* **10** (1913), 119.

[4] G. D. Bengough and D. Hanson, *J. Inst. Met.* **12** (1914), 56 (especially p. 67).

Steel containing a small quantity of iron sulphide is brittle for the same reason, the sulphide forming a web-like membrane between the grains. Many other cases exist in which a trace of a non-metal causes a normally strong metal to break with an inter-granular fracture. An experienced man, by observing the character of the fracture of a metal, can often say whether non-metallic impurities have been eliminated or not.

There is another interesting development of the conception of the inter-crystalline cement as an extremely viscous liquid. In any liquid, the resistance to change of shape which is due to the viscosity, depends on the rate at which the change of shape is brought about. The resistance is very great when the change of shape is rapid; for instance, water—a liquid of quite low viscosity—behaves almost like a rigid substance towards a rapidly moving blade. On the other hand, the resistance is greatly reduced, as the relative motion becomes small. Many amorphous substances, therefore, which are really very viscous liquids, behave towards sudden blows in a different manner to the way in which they behave towards small stresses acting for a long period. Cobbler's wax,[2] for instance, is a substance which by the slow application of force can be moulded to any form, and behaves, therefore, as a typical viscous liquid. But, if suddenly struck, it cannot undergo the plastic deformation with sufficient rapidity, and the effect of the blow is to make it fly to pieces; thus, towards sudden forces, cobbler's wax behaves like an unyielding, brittle solid.

Consider now the condition of the amorphous material that separates the grains in a pure metal. At low temperatures this behaves towards quickly applied forces as a strong cement binding the grains together. But towards a small force acting for a very long time, the behaviour may be different; in other words, the equi-cohesive temperature may depend upon the manner in which the force is applied. It has been shown that prolonged stress acting upon lead, mild steel or an alloy of aluminium may cause an inter-granular rupture, even at a comparatively low temperature, although a quickly applied force produces intra-granular fracture under otherwise similar conditions. In order to obtain the inter-granular form of fracture it is, of course, necessary for the boundaries separating the grains to be very smooth; inter-granular fracture is not usually obtained where there is any approach to interlocking between the grains.

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[1] J. O. Arnold and J. Jefferson, *Engineering*, **61** (1896), 176.

[2] A. W. Porter, *Trans. Faraday Soc.* **14** (1919), 197.

The argument stated above has been applied by Rosenhain[1] to account for the "season cracking" of brass; it is found that certain brass articles, such as cartridge cases, sometimes develop cracks on storage, although only exposed to very small forces, such as those caused by "internal stress"—a subject which will be discussed in the next chapter. The cracks only appear very slowly, and always follow the boundaries between the grains. Season cracking occurs most often when there is some slight elevation of temperature; brass cartridge cases fail in this way more commonly in India than in England. It is suggested that, towards these small forces acting for a long time, the inter-granular material behaves like a viscous liquid.

It is necessary to add, however, that Rosenhain's explanation of season-cracking, based on a "viscous flow" of the inter-granular material, has not been accepted universally.[2] It appears to be established that in almost all practical cases of season-cracking, another factor, namely the selective corrosion at the crystal-boundaries, has an important influence.[3] Certain corrosive agents, notably ammonia, a substance which is commonly present in the atmosphere, appear to attack the inter-granular material of brass in preference to the substance of the crystals themselves. Wherever by the action of ammonia the inter-granular cement is removed, the smallest forces will be sufficient to pull the grains away from each other, and the cracks which thus open between the grains allow the corrosive agent to penetrate further along the inter-granular boundary, until finally—in extreme cases—the grains are completely parted from one another.

Summary. The study of a micro-section of a piece of cast metal usually shows that it consists of polygonal grains, each grain being a separate crystal, which has grown from a single nucleus. All the atoms within a single grain are arranged according to a single mode of orientation. The boundary of the grains represent the lines along which the crystallization from different centres has met one another. Where the metal is cooled quickly in a metallic mould, practically all the nuclei are produced at the surface of the mould, and long needle-shaped crystallites perpendicular to the cooling surface result.

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[1] W. Rosenhain and S. L. Archbutt, *Proc. Roy. Soc.* **96** [A], (1919), 55. W. Rosenhain, *J. Inst. Met.* **22** (1919), 92; *Trans. Faraday Soc.* **17** (1921), 2.

[2] See W. H. Hatfield and G. L. Thirkell, *J. Inst. Met.* **22** (1919), 67. W. H. Hatfield, *Trans. Faraday Soc.* **17** (1921), 36.

[3] H. Moore, S. Beckinsale and C. E. Mallinson, *J. Inst. Met.* **25** (1921), 35. H. Moore, *Trans. Faraday Soc.* **17** (1921), 58.

A study of the pattern left on the upper surface of solidified metals, suggests that the form of the growing crystals is dendritic; this is confirmed by the examination of sections of certain alloys (bronzes, etc.). Dendritic forms are really ordinary crystals grown under circumstances especially favourable for growth at the corners rather than at the sides.

The crystal system of the metals can be arrived at by a study of the etching-pits and negative crystals produced by the corrosion of a section. X-ray analysis actually indicates the space-lattice upon which the atoms are arranged. Most metals crystallize in the cubic system (centred-cube or face-centred cubic lattices); some in the hexagonal system.

At the boundary between two grains, the atoms, having been under the simultaneous influence of crystallizing forces originating from two centres, appear to remain more or less disarranged, and the boundary layer can be regarded as amorphous. An amorphous or glassy metal should be weaker at high temperatures, and stronger at low temperatures. Hence we get inter-granular fracture at high temperatures, but intra-granular fracture at low temperatures. However, where impurities (especially non-metallic substances) have accumulated between the grains, the boundaries become surfaces of weakness, and we get inter-granular fracture even at low temperatures. Moreover it seems possible that, even in the absence of such inter-granular impurities, small forces acting for a long time may pull the grains apart at comparatively low temperatures. This view has been put forward by Rosenhain to account for inter-granular cracking ("season-cracking") in brass and other materials; but other influences, such as selective corrosion, probably play an important part in causing this form of failure.

CHAPTER II

THE STRUCTURE OF METALS AS MODIFIED BY MECHANICAL WORK

In the last chapter the structure of freshly solidified metal was described. If the metal after solidification receives any sort of deformation by mechanical means, the internal structure is necessarily modified.

Behaviour of a Metal under a Tensile Stress. In the first place, it is necessary to observe the behaviour of a piece of metal towards forces that would tend to alter its shape. The behaviour is conveniently illustrated when a piece of metal is subjected to the ordinary "tensile strength test." A test-piece is usually prepared having the shape shown in Fig. 32A. This is secured at the two ends which are then pulled apart by a gradually increasing force; during the pull the extensions caused by different values of the load, or pulling force, are recorded. Finally the specimen begins to thin out at some point, and fracture speedily follows (Fig. 32B).

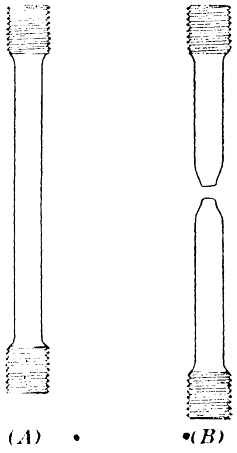

FIG. 32.

In the older forms of the testing-machine,[1] the load, which is usually applied by means of a hydraulic arrangement, must be increased in steps, the extension corresponding to each load being measured separately by the observer. After the test, a curve is plotted, showing the relation between the extension and the load. Various types of "autographic" testers have from time to time been designed, which trace the curve on paper, automatically, as the specimen is pulled out. Some of the earlier patterns are open to certain objections, but in a machine recently introduced by Dalby,[1] an intricate optical contrivance allows a curve showing the relations between load and extension to be obtained upon a photographic plate, without introducing any frictional resistance which would cause an error in the curve produced. Such a machine allows small irregularities in the curves to be detected which in the older form of machine would either have escaped observation, or would have been attributed to the imperfection of the method employed.

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[1] J. A. Ewing, "The Strength of Materials" (Cambridge University Press); C. A. M. Smith, "A Handbook of Testing Materials" (Constable).

In Fig. 33 is shown an extension curve of an imaginary material.

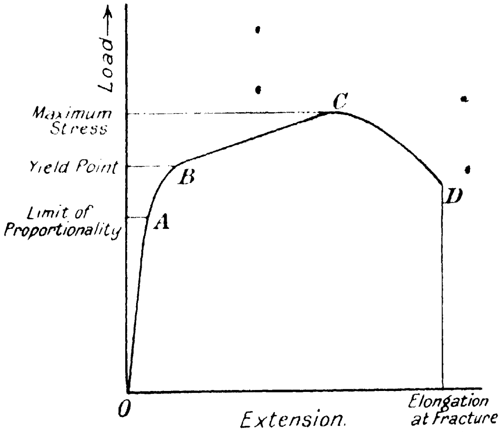

FIG. 33.—Extension Curve.

In the early part of the curve, OA, which is straight, the extension is proportional to the load applied. This portion of the curve is spoken of as being within "the range of perfect elasticity." A, the point beyond which the line ceases to be straight, is called the **limit of proportionality.**

Any extension within the range of perfect elasticity is of a temporary nature; if the pulling force were removed, the rod would return to the original length. But if the pulling force is increased further, the extension begins to rise more rapidly, and this extension is of a more lasting character and does not disappear even if the pulling force is removed; the test-piece is said to have acquired a "**permanent set.**" The point B, at which the "permanent set" first becomes appreciable, may be referred to as the **yield-point** although it should be noticed that different writers employ this term in different ways.[1] It is often assumed that the yield-point, at which a "permanent set" first appears, is identical with the "limit of proportionality" at which the elongation ceases to be proportional to the load applied. This is not necessarily the case, but in most materials the two points are close together. The vague term "elastic limit" is used by some writers as though equivalent to the "limit of proportionality," whilst others use it to imply the point at which permanent elongation first occurs.

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[1] W. E. Dalby, *J. Inst. Met.* **18** (1917), 5; *Phil. Trans.* **221** [A] (1920), 117.

Beyond the yield-point, the specimen elongates rapidly; at last the **maximum stress** (C) is reached; after this the specimen commences to thin out at one point, and, after considerable further elongation, breaks. The conditions obtaining at the instant of fracture are represented on the curve by the point D. During the final stage of extension, whilst the local thinning is occurring, the total load acting upon the specimen is usually somewhat reduced, and the curve often shows a downward trend; it should, however, be pointed out that near the place of fracture, the cross-section of the bar is continually becoming smaller, and consequently the stress *per unit area* of this portion continues to rise until fracture takes place.

It may also be remarked that, after the yield-point is passed, the metal appears to be in a plastic state, and the process of deformation under the influence of stress is a slow one, the amount of extension depending upon the time allowed. Thus the curve obtained when the stress is quickly increased (the curve of quick breaking) differs from the curve obtained when the stress is gradually increased (the curve of slow breaking).

If the stress-extension curves are plotted for a number of metals and alloys, they provide a means of comparing the mechanical properties of the different materials; the curves for certain specimens of copper, tin, brass and steel are shown in Figs. 34, 35, 36 and 37. It will be noticed that the extension corresponding to the limit of proportionality is in all cases so small, that the first part of the curve is scarcely distinguishable from the vertical axis. The curious irregularity at the yield-point shown in Fig. 37 is typical of the curves of many kinds of iron and steel.[2]

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[1] The elongation curves of steels show a very sudden extension at a certain stress, and many engineers use the word "yield-point" to denote the stress at which this sudden breakdown of the material occurs. Most other metals do not show this sudden elongation.

[2] W. E. Dalby, *J. Inst. Met.* **18** (1917), 5. Compare also A. Robertson and G. Cook, *Proc. Roy. Soc.* **88** [A] (1913), 462.

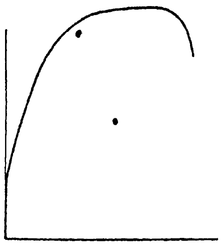
FIG. 34.—Copper.

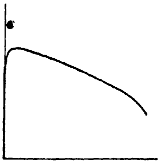
FIG. 35.—Tin.

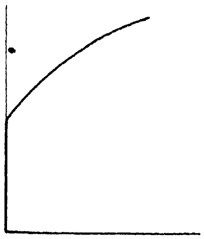
FIG. 36.—Brass.

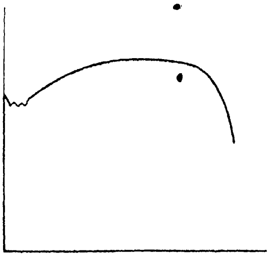
FIG. 37.—Mild Steel.

[*By permission of Professor Dalby and the Institute of Metals.*

The values of the load per unit area at the yield-point and the maximum stress are important as expressing the strength of the material in question. The yield stress represents the greatest stress which the material will stand without permanent change of shape, and without alteration in properties. The maximum stress is the greatest stress which can be withstood, under the conditions of the test, without fracture; it is often known as the "tenacity" or simply as the "tensile strength." The following table shows

Material.	Yield Stress.	Tensile Strength.	Extension.
	Tons per sq. in.	Tons per sq. in.	Per cent.
Steel, 0·1% carbon	19·65	22·7	32
Steel, 0·26% carbon	22·8	28·65	26
Steel, 0·55% carbon	27·8	43·95	16·6
Cast iron	No marked limit	13·4	0·4
Brass rod, annealed in water	15·47	30·94	19·8
Copper, electrolytic	2·63	14·12	56·7
Tin	2·8	2·8	42
Zinc	8	10·4	62

the yield stress and maximum tensile strength of a few materials; the percentage elongation of the test-piece at fracture is also added.[1]

Certain materials, like cast iron, appear to be almost incapable of permanent deformation; they fracture as soon as the elastic limit is passed. Such metals are said to be *brittle*. In a brittle metal there is no perceptible thinning out of the specimen at the point of fracture. Certain other metals can undergo a very great elongation before fracture occurs; a high value for the elongation implies that the material tested is capable of undergoing considerable change of shape by mechanical means without suffering fracture; such a material is, for example, suitable for conversion into wire by drawing through a die. There are, of course, other equally important ways of changing the shape of a metal, such as rolling, hammering, stamping and spinning; as a rule metals which are *ductile*, or capable of being drawn into wire, will readily undergo deformation in these other ways; they are, for instance, generally *malleable*, or capable of being hammered into shape, and of being rolled out into sheets without tearing or breaking. The following metals are usually considered as "ductile"; they are arranged in order so as to show the most ductile first:—

Gold, silver, platinum, iron, copper, aluminium, zinc, tin, lead.

The order of malleability is similar, but by no means identical.

Changes of Structure due to Deformation. It is now possible to consider the changes in the internal structure of the metal which has been deformed, for instance, by a tensile stress. It has been found possible to keep a polished surface of a metal specimen under observation through a microscope, whilst the specimen is actually being strained by a gradually increasing tensile force; very interesting results have thus been arrived at.[2]

Whilst the metal is merely strained to a point within the range of perfect elasticity, it suffers no visible change of structure; no doubt during the tension all the grains become very slightly elongated in the direction of the pull; but as soon as the tension is removed, the atoms fly back to the original most stable arrangement.

When, however, the metal is strained just beyond the yield-point—so that it acquires a small permanent set—the state of affairs is different. If the same grains are carefully measured before and after the pull, it can be proved that some of the grains are rendered permanently longer in the direction of pull, and shorter in the direction at right angles. Moreover, on each of the grains which has suffered a change of shape, there appears a series of dark lines known as **slip bands**. In grains where there are no slip bands, measurement shows that there is no appreciable change of shape. If the metal is strained a little further, slip bands appear in all the grains, additional slip bands being formed as the straining is continued.

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[1] The numbers are those given by W. E. Dalby, *J. Inst. Met.* **18** (1917), 20. In a later paper (*Phil. Trans.* **221** [A] (1920), 128), Prof. Dalby says that tin, zinc and copper have, strictly speaking, no range of perfect elasticity, and no definite yield-point.

[2] J. A. Ewing and W. Rosenhain, *Phil. Trans.* **193** [A] (1900), 360–363.

When deformation proceeds further, the change of structure becomes more marked. Suppose, for instance, a rod of metal is drawn out into wire, and a longitudinal section of the wire is prepared. When the section is examined under the microscope, it will appear at first that the wire is made up of a number of parallel strands, or fibres; closer investigation has shown, however, that the so-called fibres are really the greatly elongated grains.[1] Even more striking is the effect of rolling in altering the appearance of a metal as viewed in a micro-section. When an aluminium casting, consisting of equiaxed polygonal grains, is rolled out into sheet, the grains gradually become elongated in the direction of rolling, and flattened in the direction at right angles, until finally, when the sheet becomes thin, the "crystal boundaries are so close together as to give the appearance" (in a micro-section) "of a number of parallel lines running in the direction of rolling."[2]

The mechanism of the elongation of individual grains during the early stages of straining is most interesting. It is certain that, in many metals, deformation is produced by layers of the crystal gliding over one another (see Figs. 38A and B). The slip bands seen in the polished section after straining indicate the planes along which gliding has occurred; these "**gliding-planes**," as they are called, will normally be the cleavage-planes, the planes along which the natural layers of atoms composing the crystals are arranged. It has already been pointed out that the splitting of a crystal into two halves is especially easy in these directions; and it is not surprising to find that the gliding of one half upon the other is possible only along the same planes. Very careful measurements upon mildly strained lead have proved that—in that material at least—the parts of the crystal-grains between the different slip bands suffer no distortion[3]; the change in the shape of the grains as a whole is due to the different portions sliding relatively to one another.

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[1] G. T. Beilby, *Proc. Roy. Soc.* 79 [A] (1907), 463. Compare M. Polanyi, *Zeitsch. Elektrochem.* 28 (1922), 16.

[2] H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* 25 (1921), 264; the beautiful microphotos accompanying this paper show the elongation of the grains on rolling very clearly.

[3] W. Rosenhain, *J. Iron Steel Inst.* 70 (1906), 191–193.

It is, however, not possible to account for the elongation of an irregular grain satisfactorily by assuming that gliding occurs only along one set of parallel planes; it is thought that when gliding has proceeded for a minute distance along planes in one direction, as shown in Fig. 38B, further gliding occurs along other planes intersecting the first, as shown in Fig. 38C. Subsequently there may be gliding along other series of planes. Thus after straining, the original grains are split up by these intersecting gliding-planes into numerous much smaller parallelepipida. Fig. C of the frontispiece, a micro-section of strained lead, shows at least two sets of intersecting slip bands in each grain. In general the appearance of the slip bands in micro-sections of strained lead and strained iron point to the existence of four sets of gliding-planes in the same crystal, parallel to the four octahedral planes of the crystals;

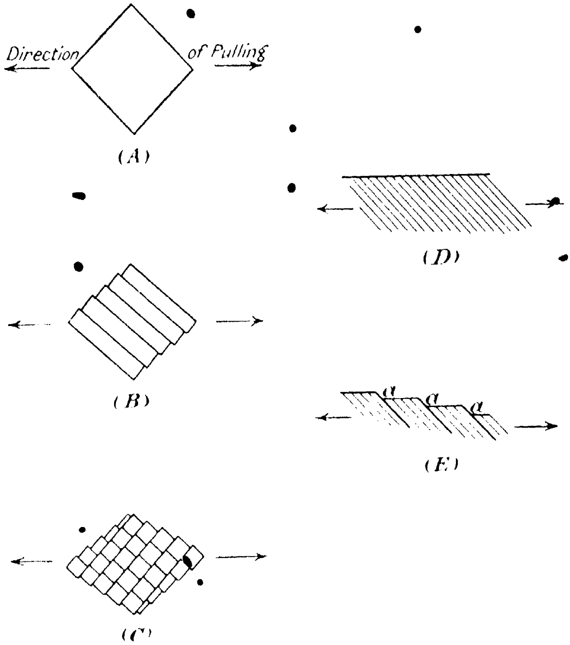

FIG. 38.—Deformation by Gliding.

in iron, slipping has also been found parallel to the three cubic planes.[1]

When a metal specimen is first ground down and polished, so as to present a flat surface (Fig. 38D) and is then strained, the formation of gliding-planes must necessarily lead to a stepped arrangement at the originally flat polished surface, as is indicated in Fig. 38E. The little facets *a*, *a*, *a*, produced by straining appear dark when the surface is viewed by vertical illumination, and hence the slip bands marking the lines of slip are normally dark. When, however, the specimen is viewed under oblique illumination, and is moved round on the microscope stage, the bands will sooner or later flash out brilliantly bright, when the light happens to strike the facets at such an angle that they reflect it up the tube. Such a phenomenon clearly indicates the "stepped" character of the strained metal.

Ductility and Crystal-structure. If we assume for a moment that the only method by which metals can be deformed is by the gliding of one layer over the other (an assumption which is not—as we shall see—quite correct), we should expect that the "ductility" of any material would be determined by the likelihood of the formation of gliding-planes in that material. It is interesting to note that a connection appears to exist between the crystal-structure and ductility of the different metals. Hull[2] has suggested a reason for the fact that most of the metals which have their atoms arranged on a face-centred cubic lattice (such as aluminium, nickel, palladium, platinum, copper, silver, gold, and lead) are remarkably ductile and malleable materials. The arrangement of the atoms in these metals is such that in any one grain, there are four different directions along which the slipping of one layer of atoms over another can easily occur; thus, there is no direction in which a shearing force can be applied, which would not be nearly parallel to one of these directions of easy gliding. In the hexagonal system of close packing, on the other hand, there appears to be only one direction suited to easy gliding, and it is noteworthy that metals with atoms arranged on the hexagonal system of packing (magnesium, zinc, and cadmium) are less ductile. Among the two most important cubic lattices, the face-centred cubic lattice seems to confer greater ductility than the centred-cube lattice (e.g. titanium, tantalum, chromium, molybdenum, tungsten, iron). In the former the packing is closer, and the distances between the atoms is less; each atom is "in touch" with twelve other atoms, as compared with eight in the case of the centred-cube lattice, although the gliding-planes are equally well defined in both methods of packing. The chance of the two layers getting out of the range of attraction during the gliding operation is presumably least in the first case. This line of thought—which is mainly due to Hull—appears to be capable of leading to most interesting results, but the theory will probably require to be extended so as to take into account the possibilities of other modes of deformation, before it will conform completely with the facts.

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[1] J. A. Ewing and W. Rosenhain, *Phil. Trans.* **193** [A] (1899), 365. J. A. Ewing, *J. Inst. Met.* **8** (1912), 14. Compare also the micro-sections of rolled β-brass given by F. Johnson, *J. Inst. Met.* **24** (1920), 301 (especially Figs. 8, 9 and 10). The mechanism of gliding in single crystals of aluminium is well illustrated by the work of H. C. H. Carpenter and C. F. Elam, *Proc. Roy. Soc.* **100** [A] (1921), 329.

[2] A. W. Hull, *Trans. Amer. Inst. Elect. Eng.* **38** (1919), 1462. Compare V. M. Goldschmidt, *Zeitsch. Metallkunde*, **13** (1921), 449.

Twinning. The formation of gliding-planes is only one method by which a grain can elongate itself in one direction and contract in another. In many metals, there is an alternative method of deformation, by means of "twinning."[1] Instead of one layer moving over the other as a whole, the atoms of every alternate layer may swing into a new orientation so that these layers become twin-lamellæ, the change being suggested in Figs. 39A and 39B. Such a rearrangement will necessarily leave the crystal shorter in one direction and longer in another, and provides a ready method of "internal buckling." Twinning is most often met with when a sudden local compression is applied to a metal. The change involves no slipping along gliding-planes, but is accomplished by the swinging of atoms throughout the whole volume of each alternate layer into a new orientation; it may, therefore, be considered a method better adapted to a sudden change of shape, and especially to deformation by local compression, or squeezing. When a piece of tin is bent sharply, twinning occurs where the tin has been compressed; on the side where the bending causes the tin to be stretched, twinning is not, as a rule, produced.[2] The bending of tin is always accompanied by a peculiar sound called the "cry of tin," which has been attributed to the movement of the atoms to their new arrangement.[3] Twinning has also been observed in large aluminium crystals which have been deformed by stretching.[4]

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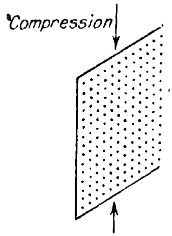
[1] The mechanism of gliding and twinning is discussed at some length by H. M. Howe, "Metallography of Steel and Cast Iron" (McGraw-Hill), Chapters 16, 18, 19, 22, 23, 24. The theories of F. Osmond and G. Cartaud, *J. Iron Steel Inst.* **71** (1906), 444, are of interest. See also J. C. W. Humfrey, *J. Inst. Met.* **14** (1915), 140. C. A. Edwards and H. C. H. Carpenter, *J. Iron Steel Inst.* **89** (1914), 138. R. Vogel, *Zeitsch. Anorg. Chem.* **117** (1921), 271.

[2] C. A. Edwards, *J. Inst. Met.* **14** (1915), 116.

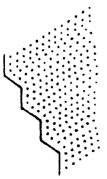
[3] P. Gaubert, *Comptes Rend.* **159** (1914), 680.

[4] H. C. H. Carpenter and C. F. Elam, *Proc. Roy. Soc.* **100** [A] (1921), 329.

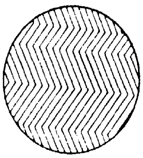
If a piece of lead is squeezed in a vice against a glass plate, twinning is produced by the pressure. The twinned structure is best seen if the metal is afterwards slightly bent in the fingers, so as to produce slip bands in the twinned metal. When the specimen is examined under the microscope, the slip bands are found to proceed in a zigzag manner across the grains as shown in Fig. 39c; this clearly indicates that the arrangement of atoms in alternate layers is different.[1] A similar effect can be produced in nickel and copper.



(*A*) Arrangement before Pressure.



(*B*) Arrangement after Pressure.



(*C*) Actual Course of Slip Bands in Strained Lead or Nickel.

FIG. 39.—Deformation by Twinning.

Other Modes of Deformation. Two modes of deformation have already been suggested, namely *gliding*, which is generally observed in metals subjected to a uniform tensile stress, and *twinning*, which is often met with in metals subjected to a localized compressional stress. Cases exist, however, where a metal has undergone considerable deformation, but where it would be difficult to account for the whole of the deformation by gliding or twinning alone. Where a slab of cast metal made up of polygonal grains is subjected to rolling, the grains become gradually elongated in the direction of rolling, and are reduced in the direction at right angles; in some cases, the reduction may proceed until the individual grains are mere thin flakes.[2] Adcock has recently prepared some etched micro-sections of the rolled alloy, cupro-nickel, which make it clear that in many of the elongated grains the gliding of one layer over another has occurred; but in addition the sections show that in certain places the whole crystal has been "bent."[1] It is difficult to see how this could be otherwise, since the elongation of a single crystal by a process of simple gliding must produce a "stepped" outline at the boundary of the grains, and in general the "steps" produced at the edge of two adjacent grains will not "fit in" with one another. Hence one must expect considerable disorganization of the atoms at the grain-boundaries, which in extreme cases may amount to the total destruction of the ordered arrangement, and the production of an "amorphous" layer of considerable thickness.[2] In cupro-nickel there appears also to be considerable disorganization along the planes of gliding; it is probably on account of the production of more or less amorphous material where one portion has glided over another that the gliding-planes appear as dark lines on the etched sections.

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[1] J. A. Ewing and W. Rosenhain, *Phil. Trans.* **193** [A] (1899), 368. C. A. Edwards and H. C. H. Carpenter, *J. Iron Steel Inst.* **89** (1914), 138, especially micro-sections 3 and 15.

[2] See the sections of rolled aluminium given by H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* **25** (1921), 259.

It is difficult to avoid the conclusion that the atoms, which in the original cast state, are accurately alligned upon a space lattice, can be gradually forced from their stable positions, until at points where the disorganization is very great (e.g. at the grain-boundaries) they are arranged in a more or less disordered manner, all traces of the original space-lattice having disappeared. According to this view, we get a passage from the crystalline state to a more or less amorphous state, but the passage is probably a gradual one.[3] Where the degree of deformation is not too great, the atoms may be regarded as being arrayed still upon a space-lattice, but it is a distorted space-lattice.[4]

Of course the arrangement of atoms on a distorted space-lattice is an unstable arrangement, and if it were possible, the atoms would tend to spring back to their stable arrangement on an undistorted lattice. Nevertheless in a piece of metal which has been suffered deformation by mechanical forces, the space-lattice in certain regions appears to remain distorted even after the external deforming forces have been removed. For instance, in one strained crystal-grain the atoms may be prevented from jumping back to their stable arrangement, since the existence of the contiguous grains precludes the change of shape which the return to the stable arrangement would involve. Thus in a deformed metal we continually meet with **internal stresses.** These internal stresses are of great practical importance; where the grains on the outside of a metallic object are in a state of tension, the individual grains may actually, in the course of time, become parted from one another as a result of the internal stress—especially if a reagent is present which has a specific corrosive action on the inter-granular material; the phenomenon known as "season-cracking," discussed in the last chapter, is the result. We shall return to the subject in connection with the "annealing" of metals.

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[1] F. Adcock, *J. Inst. Met.* **27** (1922), 73.

[2] Compare Z. Jeffries and R. S. Archer, *Met. Chem. Eng.* **25** (1921), 697, especially p. 704.

[3] Compare the views of J. Czochralski, *Int. Zeitsch. Met.* **8** (1916), 22, of G. Masing, *Zeitsch. Metallkunde*, **12** (1920), 457, and of P. Gaubert, *Comptes Rend.* **173** (1921), 1089.

[4] Evidence that a space-lattice may persist in a distorted form in a deformed crystal is believed by many physicists to be provided by an optical study of some plastic needle-shaped crystals of ammonium nitrate, which may be bent into loops or circles by slow pressure with the fingers. See W. N. Bond, *Phil. Mag.* **41** (1921), 1. A. W. Porter, *Trans. Faraday Soc.* **17** (1921), 66. T. M. Lowry, *Trans. Faraday Soc.* **17** (1921), 66, 67.

Very interesting information regarding the arrangement of the atoms in deformed metals is provided by recent studies of rolled or drawn metals carried out by means of the X-rays.[1] Even after suffering very great reduction by means of rolling or drawing, the metals give X-ray patterns, which show that the atoms are—at least in some parts of the materials—arranged in an orderly manner. But the orientation of the rows of atoms in the rolled or drawn specimens is not fortuitous (as in the cast or annealed state), but is related to the direction of rolling or drawing—as indeed is to be expected. Thus in drawn tungsten wire, all the crystal-grains are arranged with the so-called [110] direction (i.e. the direction defined by the diagonals of the faces of the elementary cubes) parallel to the length of the wire. The same is true of wire made of iron or molybdenum, metals which (like tungsten) have their atoms arranged on a centred cube lattice; for copper and aluminium, in which the atoms lie on a face-centred lattice, another slightly different rule applies.

Comparative Strength of Coarse and Fine-grained Metal.

It has long been known that a fine-grained specimen of metal is less liable to fail than a specimen of the same metal in which the grains are large. It is indeed easy to understand why a specimen containing very large grains should be fragile. Imagine a bar composed of grains of such a size that a single crystal runs through the whole diameter of the bar. In such a case, the cleavage direction is constant throughout the thickness of the bar, and a single sudden shock in the right direction may cause the bar to split in two. In a fine-grained bar of the same size, however, the cleavage direction will vary slightly as one passes from one grain to the next. Therefore, any line of possible fracture will not be quite straight, and it will require a much greater shock to bring the simultaneous splitting of so many different grains, so as to produce a crack right across the cross-section of the bar.[1] Hence, towards a shock, the fine-grained material will be the less fragile.

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[1] M. Ettisch, M. Polanyi and K. Weissenberg, *Zeitsch. Phys. Chem.* 99 (1921), 332. M. Polanyi, *Zeitsch. Elektrochem.* **28** (1922), 16. E. C. Bain and Z. Jeffries, *Met. Chem. Eng.* **25** (1921), 775. H. C. Burger, *Phys. Zeitsch* **23** (1922), 14. S. Nishakawa and G. Asahara, *Phys. Rev.* **15** (1920), 38. The last paper describes the changes in X-ray pattern which occur on annealing the rolled metal, or (in the case of certain soft metals) on mere storage. Compare the X-ray study of the compression of sodium chloride by A. F. Goffe and M. V. Kirpitcheva, *Phil. Mag.* **43** (1922), 204.

Towards a tensile stress the behaviour of a fine-grained specimen will also be different from that of a coarse-grained specimen. Consider the pulling out of a ductile metal. If the specimen of the metal consists of a single crystal, the gliding can proceed without hindrance. But if the metal consists of numerous crystals, the movement of the slices of any particular crystal over one another will be restrained by the presence of the other crystals in contact with the first. If the crystals in the specimen are very numerous the resistance to pulling will be greatest, and consequently a fine-grained specimen of metal is stronger and withstands the action of deforming forces better than a coarse-grained specimen.[2] This general statement, however, applies only to temperatures below the equi-cohesive temperature; below that temperature, the inter-granular amorphous material is stronger than the crystals themselves, and deformation occurs by gliding within the crystals; consequently, as just shown, a fine-grained metal will be stronger than a coarse-grained. On the other hand, above the equi-cohesive temperature the inter-granular matter begins to soften, and, since the number of inter-granular boundaries in the specimen will be greatest in the fine-grained material, the coarse-grained sample will be the stronger.[3]

The equi-cohesive temperature is, in fact, most easily determined by finding the point at which a fine and coarse sample of the same metal withstands deformation equally well. The table below shows the approximate equi-cohesive temperatures of five metals obtained in this way. It cannot be said that the values are known with any accuracy.

Since the strength of amorphous material depends on the *rate* at which the force is applied, and the strength of crystalline material depends on the *direction* in which the force is applied, it is clear that the equi-cohesive temperature, although a useful rough conception, is not an exact physical constant.

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[1] The characteristics of a shock fracture are described by W. Rosenhain, *J. Iron Steel Inst.* **70** (1906), 222.

[2] Z. Jeffries and R. S. Archer, *Met. Chem. Eng.* **24** (1921), 1057; **25** (1921), 697.

[3] Z. Jeffries, *J. Amer. Inst. Met.* **11** (1917–18), 300.

The equi-cohesive temperature of copper, which is added, was obtained in a different way, being the temperature above which intra-granular fracture was observed to be replaced by fracture of the inter-granular type; this number is, therefore, not strictly comparable with the others.

Metal.	Equi-Cohesive Temperature.	Melting Point.
Iron	550–660° [1]	1,530° C.
Tungsten	1,350° [1]	3,540°
Platinum	525–550° [1]	1,755°
Gold	275–300° [1]	1,063°
Silver	250–275° [1]	962°
Copper	between 710 and 719 [2]	1,083°

Alteration of Properties by Mechanical Work. It has long been known that metals are made harder, stronger and less ductile by mechanical deformation at low temperatures. This fact can now be explained. When a metal is deformed, each grain is subdivided into a large number of parts by various sets of intersecting gliding-planes. It is very possible that after deformation, the atoms on each side of a gliding-plane will be in a somewhat disordered state, and will lose their accurate crystalline orientation. We may express this by saying that a layer of more or less amorphous material is formed along each gliding-plane. In any case, it is almost certain that disorganization must occur at the boundaries of each grain during elongation, the original amorphous layer between the grains thus becoming thicker; it has already been pointed out that this disorganization at the boundaries is absolutely necessary, because the "steps" which would be formed by gliding in adjacent crystals will not—in general—"fit into" one another. The process of deformation may therefore be said to be accompanied by the **amorphization** of the metal.[3] Below the equi-cohesive temperature, the result of the increase in the amount of disorganized material present will be to increase the limit of proportionality and yield-point, and also, to a smaller extent, the maximum stress. The ductility is lowered, because, as the crystals are shattered, the possibility of forming new gliding-planes is lessened; and, as the power of accommodation to sudden forces by stretching or yielding becomes reduced, the material not infrequently becomes brittle.

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[1] Z. Jeffries, *J. Amer. Inst. Met.* **11** (1917–18), 300.

[2] G. D. Bengough and D. Hanson, *J. Inst. Met.* **12** (1914), 67.

[3] The American writers speak of "amorphization," whilst some German writers use the word "decrystallization" in a rather similar sense.

Where deformation is accompanied by twinning instead of slipping, a rather similar effect is produced. In a twinned crystal, the cleavage direction changes as one passes from one thin lamella to the next. Therefore, a highly-twinned mass must always be more unyielding than an untwinned mass. Moreover, the process of twinning will be accompanied by a certain amount of disorganization of the atoms at the boundaries of the grains. It should be added, however, that the hardening effect of twinning is generally less pronounced than that of slipping.

There are various shades of opinion regarding the effect of deformation upon the character of a metal. Beilby[1] thinks that a distinct amorphous phase is formed which has different properties from the crystalline metal. J. Johnson[2] goes further, and—treating the amorphous metal as a true liquid—proceeds to explain how the melting-point of the metal can be lowered to ordinary temperatures by a "non-homogeneous" pressure, such as is needed to cause deformation. Whether Johnson's arguments are sound or not, there is no doubt that metals with low natural melting-points are, for the most part, much softer (that is, they can be deformed by means of a much smaller pressure) than those with high melting-points.[3] The views of Beilby and of Johnson have, however, been attacked by Tammann,[4] who objects to the notion of a metal "melting" below the true melting temperature.

It appears quite probable that at points where the disturbance is strongest, the crystalline metal is converted to a state which is entirely structureless and amorphous, and which may correctly be regarded as that of a super-cooled liquid. At other points, however, the crystalline structure, although modified, is not entirely destroyed. The crystals are shattered and broken up into fragments; and possibly even in these fragments the space-lattice may be strained, the atoms being forced out of their true alignment, or perhaps forced to vibrate more in some planes than in others.[5] Such a state of affairs would hinder the formation of fresh gliding-planes, and would account for the unyielding character of the strained material.

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[1] G. T. Beilby, *Phil. Mag.* **8** (1904), 258. G. T. Beilby and H. N. Beilby, *Proc. Roy. Soc.* **76** [A] (1905), 462.

[3] J. Johnston and L. H. Adams, *J. Amer. Chem. Soc.* **34** (1912), 563. J. Johnston, *J. Amer. Chem. Soc.* **34** (1912), 788.

[3] N. Kurnakow and S. Żemczużny, *Zeitsch. Anorg. Chem.* **64** (1909), 177.

[4] G. Tammann, *Zeitsch. Elektrochem.* **18** (1912), 584; *Zeitsch. Anorg. Chem.* **92** (1915), 37. See also E. Heyn, *Int. Ass. Test. Mat., 6th Congress* (1912), First Section, II, i., p. 43.

[5] Interesting views of the changes caused by cold work are advanced by W. von Moellendorff, *Int. Zeitsch. Met.* **6** (1914), 44, and by A. McCance, *Trans. Faraday Soc.* **10** (1914–15), 257.

Whatever view is taken of the theory of the process, there is no doubt about the practical effects upon metals of mechanical work at low temperatures.[1] When copper is drawn out into wire "in the cold" a great increase in the tensile strength is noticed; the cold-rolling of brass and other materials into sheets or strips causes an increase in the hardness. A metal like aluminium may be very perceptibly hardened by being hammered in the cold. The punching of a hole in a metal plate often causes considerable hardness—sometimes accompanied by brittleness—around the opening. The properties of a metal are likewise greatly modified, when it is reduced to the state of filings.[2]

Indeed, the cold-worked and annealed forms of the same metal seem to behave as though they were two different substances; a thermo-couple in which the two elements consist of cold-worked silver wire and annealed silver wire gives a very appreciable E.M.F.[3] Further, the electrical conductivity changes when a metal suffers deformation in the cold; the conductivity of annealed copper wire is 2·7 per cent. higher than that of the cold-drawn variety.[4]

In addition, the chemical properties of a cold-worked metal differ from those of the annealed variety. This is not altogether surprising. Since the chaotic arrangement of atoms is less stable than the crystalline arrangement, it is to be expected that the amorphous or pseudo-amorphous metal will be less resistant towards chemical action. It is even thought possible by Beilby to separate the crystalline metal from an aggregate containing both varieties by dissolving the amorphous phase in a suitable reagent. For instance, if gold is beaten out into the finest gold-leaf, most of it is converted into an apparently amorphous condition. On etching it with potassium cyanide, this "amorphous" gold is dissolved away, but minute units of crystalline matter which have survived the drastic treatment are left undissolved.[5]

If the "amorphous" or disorganized material is more susceptible to attack than crystalline material, it is to be expected that a cold-worked metal will appear to be a less resistant—or less "noble"—

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[1] A good account of the effect of cold work on metals is given by D. R. Pye, *J. Inst. Met.* **6** (1911), 165; O. W. Ellis, *J. Inst. Met.* **21** (1919), 319.

[2] Compare T. M. Lowry and R. G. Parker, *Trans. Chem. Soc.* **107** (1915), 1005.

[3] G. T. Beilby, *Proc. Roy. Soc.* **79** [A] (1907), 474.

[4] F. A. Wolff and J. H. Dellinger, *U.S. Bur. Stand. Bull.* **7** (1911), 118.

[5] G. T. Beilby, *Proc. Roy. Soc.* **79** [A] (1907), 465. The existence of crystalline units in gold leaf, that is of groups of atoms retaining an ordered arrangement, is confirmed by an X-ray study of gold leaf; Mr. A. Müller has very kindly prepared for me a röntgenogram of gold leaf which shows lines which would appear to indicate the presence of a crystalline structure in the leaf. See U. R. Evans, *J. Inst. Met.* **27** (1922), 139.

substance than the same metal after annealing. This is, in general, the case,[1] and is a matter of considerable importance in the science of electro-chemistry. It has been stated, however, that, in a few metals, such as copper and aluminium, cold-work renders the metals less susceptible to the attack of certain etching agents.[2]

We may summarize the matter by saying that a cold-worked metal differs from an annealed metal not only in *mechanical* properties, but in *chemical, electro-chemical, electrical* and *thermo-electric* properties also.

Failure of Metals subjected to alternating Stress. When a piece of metal is subjected to alternating stress, that is to the application of tension and compression alternately, it is liable, after withstanding several thousands of these alternations, to become brittle and to fracture. Such cases of failure—which may occur when the stress applied is very much less than the maximum stress as determined by the ordinary tensile tests—are well known to engineers, who ascribe them to "fatigue." It has been shown that there is for each material a limit known as the "endurance limit." An alternating stress below the endurance limit will never cause failure even though applied for many millions of alternations. But any stress above this limit will finally cause failure; and the number of alternations needed to cause failure decreases as we pass farther and farther above the "endurance limit."

The fatigue of a metal appears to be yet another example of the radicle change in properties brought about by repeated cold-work. The matter has been studied by examining the specimen at intervals during an alternating stress test. Slip bands may be seen on the specimen after a few alternations. After further applications of stress the slip bands increase in number and some of them become broader, and finally develop—probably after many thousands of alternations—into cracks; when the cracks in neighbouring grains meet one another, so as to form one long crack through the whole specimen, fracture will occur.[3]

Where a specimen of metal contains internal cavities, which cause the stress upon the portions of metal surrounding them to be greater than elsewhere, the damage will often commence at the cavities, and will gradually spread throughout the material.

If the failure of metals by fatigue depends on the formation of slip bands, it is to be expected that the straining of the metal within the range of perfect elasticity—which produces no slip-bands—will be incapable of causing failure by fatigue. One authority has suggested that the "endurance limit" is identical with the "limit of proportionality." [1]

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[1] W. H. Walker and C. Dill, *Trans. Amer. Electrochem. Soc.* **11** (1907), 153.

[2] J. Czochralski, *Stahl u. Eisen*, **35** (1915), 1074.

[3] J. A. Ewing and J. C. W. Humphrey, *Phil. Trans.* **200** [A] (1903), 241. Other interesting work on fatigue is described by B. Hopkinson, *Proc. Roy. Soc.* **86** [A] (1911–12), 131. B. Hopkinson and G. T. Williams, *Proc. Roy. Soc.* **87** [A] (1912), 502.

There is—or, at least, there was—a common belief that metals become crystalline under an alternating stress. This is wrong. The fracture caused by fatigue sometimes "shows up" the crystalline structure of metals particularly well, but the crystalline structure was there long before the stress began.[2]

Hardness of Metals. Many of the forces to which a body comes to be subjected tend to produce alteration in shape—not to the body as a whole—but to the surface of the body only, producing scratches, indentations or perhaps general wear. The power to withstand these superficial changes is vaguely termed the *hardness* of the body. If the surface layer of the material is the same as that of the interior, the hardness of the body should be closely connected with the strength, as determined, for instance, by the tensile tests. In many instances, this is found to be the case. Often, however, the structure or composition at a surface is different from that in the interior, and in such cases it is not to be expected that there will be any connection between the hardness of the surface and the strength of the material as a whole.

Various methods of measuring hardness have been devised. In the **Brinell test,** a steel ball is pressed down with a known force upon the surface to be tested; the diameter of the circular impression produced is then measured, and from this it is easy to calculate the stress (or force per unit area) which the metal withstood when the ball ceased to penetrate further into it. If the material of the surface is similar to that of the interior, this should be roughly proportional with the *maximum stress* obtained on the tensile testing machine, and generally speaking this has been found to be the case.[3]

Another principle is embodied in the **Shore test.**[4] Here a steel ball is dropped from a known height on to the surface to be tested, and the height to which it rebounds is measured. The harder the material, the greater the rebound. The height of rebound is expressed as a percentage of the height from which the ball was dropped; the percentage numbers obtained are under favourable circumstances roughly proportional to the *elastic limit* as measured in the tensile test.

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[1] W. E. Dalby, *Phil. Trans.* **221** [A] (1920), 137. Compare C. E. Stromeyer, *Proc. Roy. Soc.* **90** [A] (1914), 411, who measures the endurance limit by determining the stress at which the specimen undergoing alternations becomes perceptibly heated; this will be the stress at which the specimen begins to undergo *plastic*, as opposed to *elastic*, deformation.

[2] See F. C. A. H. Lantsberry, *Engineer*, **119** (1915), 68.

[3] H. Le Chatelier, *Rev. Met.* **3** (1906), 689. Further investigations regarding the Brinell method are described by A. Wahlberg, *J. Iron Steel Inst.* **59** (1901), 243.

[4] A. F. Shore, *Amer. Machinist*, **30** (1907), 747.

A third type of method is employed in **Turner's sclerometer.** A weighted diamond point is moved over the surface to be tested. The weight needed to produce a scratch of standard appearance is determined; this is a measure of the hardness.

It will be evident that the term hardness is not an exact one [1]; it is used by some persons to mean "resistance to indentation," by others to mean "resistance to scratching"; others, again, employ it to signify "resistance to general wear," whilst some even regard the term as synonymous with "cutting power." In some classes of materials, the degree of resistance to one sort of deformation may be an indication of the resistance to another sort; but this is by no means always true. Among the steels, for instance, the factor required to convert the "Brinell number" to the "Shore number" varies considerably according to the type of steel tested.[2]

If it is desired to measure resistance to indentation, the Brinell test should be used; if resistance to scratching, the Turner test is available. Where, however, the resistance to general wear of a material is to be arrived at, it is necessary to construct some machine which will reproduce the conditions to which the material will be subjected in actual use, and then to measure the amount of metal worn away in a given time. Sanniter [3] has devised such a machine for measuring the wear of steel rails. It is noteworthy that the type of steel found by Sanniter to give the best results in the wearing test, has quite a low hardness number when tested by the Brinell method. Similarly, to estimate the cutting power of a steel, the only method which is of real use is to prepare a cutting edge and determine its efficiency by means of a lathe test; the Brinell and Shore hardness numbers give little indication of the value of a material for this purpose.[4]

Beilby's Theory of Polishing. Another example of deformation restricted to the surface of metal is provided by the process of polishing; it differs from the examples considered above in that polishing renders the surface smoother, instead of less smooth.

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[1] T. Turner, *J. Inst. Met.* **18** (1917), 87. J. W. Craggs, *J. Soc. Chem. Ind.* **37** (1918), 43 T.

[2] A. F. Shore, *J. Iron Steel Inst.* 98 (1918), 59. Sir R. Hadfield, *J. Iron Steel Inst.* **98** (1918), 69.

[3] E. H. Sanniter, *J. Iron Steel Inst.* **78** (1908), 73; *Int. Ass. Test. Mat. 6th Congress* (1912), *First Section*, III, i. The connection between resistance to wear and hardness is discussed also by T. Turner, *J. Inst. Met.* **18** (1917), 90; F. C. A. H. Lantsberry, *J. Inst. Met.* **18** (1917), 112.

[4] J. O. Arnold, *J. Iron Steel Inst.* **93** (1916), 102.

At one time polishing was regarded as a kind of minute abrasion; the projecting portions of the rough surface were, it was thought, worn away by the action of the polishing material. It has, however, been shown that polishing generally consists in making the material flow down from the minute projections on the surface, and fill up, or cover up, the depressions. Thus, when the polishing is complete, the whole surface is covered over with a smooth vitreous layer of more or less "amorphous" metal, produced by the action of cold work, the layer being often spoken of as the "amorphous varnish."

The formation of this surface film depends very largely on the nature of the polishing powder used. When ferric oxide (rouge) is rubbed over the surface, the particles exert a remarkable drag upon the surface atoms of the metal, causing rapid "smearing." Aluminium oxide exerts a smaller drag upon the metal, whilst magnesium oxide has often very little true polishing action, behaving more like a fine abrasive.[1]

Presumably there exists a greater attractive force between the atoms composing the rouge particles and the surface atoms of the metal, than exists between the atoms of the magnesia particles and those of the metal. This is confirmed by the fact that a certain amount of rouge is actually retained in the surface film. Silver polished by rouge has a darker lustre than silver polished with magnesia; occasionally, moreover, where the rouge used is too soft (not having been heated sufficiently during manufacture) the silver after some time develops minute black dots on the surface, which are nothing else than small particles of ferric oxide.[2]

The nature of the polishing process is well shown by some experiments due to Beilby.[3] A piece of antimony is ground down with emery paper, the final grinding being carried out by emery of extreme fineness. Nevertheless, the surface can be seen under the microscope to be covered with striations, representing the minute furrows left by the emery. It is now polished with wash-leather sprinkled with rouge; on examination under the microscope the striations have for the most part disappeared, a film of metal having spread over the whole surface, sometimes filling the furrows and sometimes bridging over them. When, however, the metal is etched with potassium cyanide solution, the striations reappear;

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[1] W. Rosenhain, *J. Iron Steel Inst.* **70** (1906), 197; especially footnote.

[2] See W. Rosenhain, *Engineering*, **96** (1913), 510.

[3] G. T. Beilby, *Proc. Roy. Soc.* **72** (1903–4), 218. See also Lord Rayleigh, *Proc. Opt. Conv.* (1905) 73; W. Rosenhain, *Proc. Opt. Conv.* (1905), 76.

the potassium cyanide dissolves the amorphous film and reveals the furrows which were previously hidden behind it. Incidentally, the experiment affords an illustration of the preferential attack of an etching agent upon the amorphous phase, the crystalline metal being almost untouched by the cyanide.

Another interesting experiment concerns the polishing of a specimen of copper, the surface of which contains numerous pits, due to gas included in the metal at the time of casting.[1] When the surface is polished the pits disappear, the amorphous film having flowed over and hidden them. By cautiously etching away part of the amorphous film, Beilby reached a stage when the remaining portion of the film was so thin as to be transparent, and the pits were then visible through the film. When the etching was carried farther, the rest of the film was removed, and the pits reopened, with the same appearance as at the start.

Various other operations of mechanical work are believed to cause the presence of a hard glass-like film upon the surface of metals, particularly those of drawing and rolling at low temperatures. Cold-drawn copper wire is stronger and harder than hot-drawn wire of the same composition. Many authorities have long believed that the added strength of the cold-drawn wire is due to a hard glassy skin of "amorphous" copper upon the surface. Doubt has, however, been thrown on this view by recent investigations[2]; the hard skin, where it exists at all, appears to be due to oxide scale rolled into the wire.[3]

In the case of a brass tube, on the other hand, the existence of an apparently amorphous surface layer appears to be established. It has, in fact, been found possible to strip the layer from the granular material below, by the action of dilute ammonium chloride.[4] The layer proper is structureless, but a good deal of crushed or sub-crystalline material from below is usually found adhering to the lower surface.

Annealing. Mechanical deformation, as has been shown, causes the atoms of cast metals to abandon the orderly array in perfect crystals of appreciable size which represents the condition of maximum stability; even though the crystal structure may not —in any case—be entirely destroyed, the crystals are shattered into small fragments, and the lattice is probably distorted and even in places obliterated. The final chaotic state represents a much less stable arrangement than the first. It would seem natural therefore that, as soon as the external stress is removed, the atoms should commence to rearrange themselves in a stable crystal array. In soft metals, like lead and tin, the atoms have sufficient freedom of movement at ordinary temperatures for this reorganization to commence spontaneously. In other metals, it is necessary to raise the temperature before the atoms acquire the necessary mobility to revert to the most stable arrangement. The process of maintaining a piece of metal at an elevated temperature so as to remove the effects of strain is spoken of as "**annealing.**"

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[1] G. T. Beilby, *Proc. Roy. Soc.* **89** [A] (1914), 593.

[2] E. H. Pierce, *Proc. Amer. Soc. Test. Mat.* **17** (1917), 115.

[3] L. Addicks, *Proc. Amer. Soc. Test. Mat.* **17** (1917), 122.

[4] G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 80.

The first effect of annealing at a fairly low temperature is simply to remove the internal stresses which are always present in deformed metals; it is found that the annealing of cold-worked brass at a low temperature (200–250° C.) is capable of removing entirely the nternal stresses, which predispose the brass to season-cracking, without altering perceptibly the special hardness which has been caused by the cold-work.[1] Apparently in the portions where the atoms are only slightly removed from their true positions on the pace-lattice (thus producing the internal stresses), the atoms revert to the most stable arrangement, and the distortion of the attice disappears.

More vigorous annealing produces other effects. The metal oses its acquired hardness; it ceases to be brittle, and becomes ductile once more. The elastic limit and yield-point, which were o much raised by deformation, are again greatly reduced. This marked change of physical properties is accompanied by a change of structure—namely by the growth of certain crystals at the xpense of others, and in some cases by the appearance of fresh rystals in the material. Apparently in the portions where the original crystals have become broken up or disorganized as a result of the deformation, the atoms commence to rearrange themselves n perfect crystal-array, but the orientation will in general not be he same as that existing before the metal was strained. Where he deformation of the metal as a whole has been small, certain rains which have escaped serious disorganization may act as nuclei pon which the atoms of the shattered material all around them an commence to rearrange themselves. In such a case, these rains will commence to grow outwards into the shattered material round them, and we get the phenomenon which Prof. Carpenter nd Miss Elam have named **grain-growth.** But where the disrganization of the crystal-structure is great (e.g. at the grain-oundaries), crystallization may commence from nuclei which rise (apparently spontaneously) in the disordered material (just as crystallites appear spontaneously in a glass when it undergoes devitrification); this leads to the appearance of entirely fresh crystals, and the phenomenon has been termed **recrystallization.**

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[1] H. Moore and S. Beckinsale, *J. Inst. Met.* 23 (1920), 225.

The effect of annealing upon structure is well illustrated by some experiments upon zinc.[1] When a cast piece of zinc is strained by compression in a vice, the beautiful granular structure is gradually obliterated. When the stress applied has been but feeble, the outlines of the original grains can still be distinguished in a section, although the grains are hopelessly broken up: when a greater stress is applied, all signs of the original granular structure disappears, and the appearance in an ordinary micro-section becomes almost homogeneous. If the strained metal is annealed, however, the structure once more reverts to that of large equiaxed polygonal grains with smooth well-marked boundaries.

It is not true, however, to say that a piece of cast metal which has been deformed and then annealed, returns entirely to the original structure. For, in the first place, the grain-size after annealing is often not the same as that of the cast metal; sometimes it is coarser—which is liable to weaken the article. Secondly, the grains of the annealed metal are not always accurately equiaxed, being often elongated in one direction; where, for instance, the article had been deformed by rolling, the grains will sometimes be longest in the direction of rolling, even after annealing. Thirdly, in some metals, twinning can be seen in the metal after annealing, although absent in the original casting. Finally, it may be remarked that the boundaries of the grains shown in sections of strained and annealed specimens are usually much smoother and straighter than in ordinary cast metals.

The grain-size of the metal after annealing is affected by at least four factors:—

(1) the degree of deformation,
(2) the temperature of annealing,
(3) the duration of annealing,
and (4) the presence or absence of obstructive impurities.

These factors will be discussed in turn.

The effect of the degree of deformation on grain-size is shown clearly in cases where a piece of metal has been deformed by a non-uniform stress. For instance, if the surface of a piece of steel is indented by pressing a hard ball into it, and is then annealed, a section at right angles to the surface shows three zones (Fig. 40)[2]:—

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[1] G. Timoféef, *Rev. Mét.* **11** (1914), 127; *Comptes Rend.* **155** (1912), 430.
[2] A. Sauveur, *Int. Ass. Test. Mat. 6th Congress* (1912), *First Section*, II. 6.

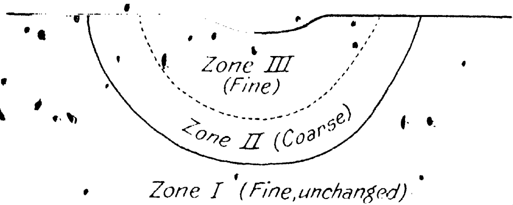

FIG. 40.—Zones produced on annealing a non-uniformly strained piece of Metal.

Zone I. The main body of the steel far from the indentation has clearly been subjected to a very small stress, and naturally has undergone *no apparent change*.

Zone II, rather closer to the indentation, has clearly been subjected to a greater stress ; here we find *very big grains*, very much bigger than those of the original steel before straining.

Zone III, which is next to the indentation, where the stress must have been greatest, has, however, *much smaller grains*, the general appearance being actually very similar to that of the unchanged Zone I.

Zones II and III pass insensibly into one another, the grains becoming gradually smaller as they approach the indentation.

It may appear anomalous that whilst a moderate stress causes so great an increase in the size of the grains, a much greater stress causes practically no alteration in the grain-size. If, however, it is borne in mind that crystallization from the strained disordered state—like the crystallization from the fused state—probably starts from nuclei, a regularity is at once apparent. For the phenomenon can be tabulated thus :—

Zone I. Stress very small. *No fresh crystallization* ; grains remain *small*.

Zone II. Stress moderate. Crystallization from a *few nuclei* ; hence very *large* grains.

Zone III. Stress high. Crystallization from *many nuclei* ; hence *small* grains are produced.

To express the matter in a single sentence : if an unequally strained piece of metal be annealed, there will be a zone of coarse crystals between the recrystallized and unchanged portions.

The expression " crystallization from nuclei " is intended to include the two possible modes of crystallization which, as already explained, may occur during annealing. Our knowledge of these is largely due to the recent experiments of Prof. Carpenter and Miss Elam.[1] They are :—

(*a*) **Crystal-growth,** characteristic of annealing after *mild deformation.* This normally leads to an *increase* of grain-size.

(*b*) **Recrystallization,** characteristic of annealing after *great deformation.* This may lead to a *decrease* of grain-size.

(*a*) The first phenomenon, namely **crystal-growth,** is conveniently studied in tin containing 1½ per cent. of antimony. If a polished and etched section of this alloy (the preparation is by no means easy) is heated under conditions which give rise to crystal-growth, and then cooled, the new positions of the boundaries of the various grains are clearly shown by well-defined lines: the lines really represent differences of level between the grains—presumably due to some volume-change connected with the cooling-process. The lines marking the original position of the boundaries are not however obliterated, and, if the specimen is heated for five or six short periods, being cooled between each, we shall get five or six lines marking the positions of the boundary at the end of each "heat." Such an alloy clearly furnishes a ready means of arriving at the laws of crystal-growth.

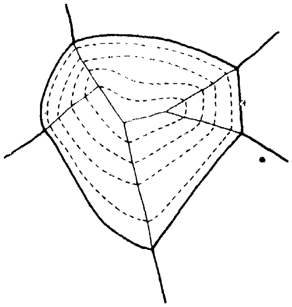

FIG. 41.—Invasion of a Crystal by its Neighbours as shown by the Work of Carpenter and Elam.

Boundaries before annealing ——

Boundaries after first, second, third, and fourth heat - - - -

Final Boundaries — —

It has been discovered in this way that, during the annealing process, the boundary separating two adjacent grains often advances as a whole, in one direction or the other, so that one grain grows larger, whilst its neighbour grows smaller. Sometimes a grain may be invaded by all its neighbours, and will finally disappear altogether. Such a case is shown in Fig. 41; here the central grain had originally the outline shown by the thick line, but, on succeeding "heats" its five neighbours advanced into it (the position of the "frontier" after each "advance" being shown by the broken lines) and their advance has only ceased when they met one another at the positions indicated by the thin unbroken lines. Sometimes, however, one grain may be invading a neighbour on one side, whilst it is itself being invaded by another grain on another side. Occasionally, a boundary may remain stationary for one or more "heats," and will commence to move forward on the next "heat."

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[1] H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* **24** (1920), 83; **25** (1921), 259; *Proc. Roy. Soc.* **100** [A] (1921), 329.

The theory of grain-growth is still a matter about which different views are held. It seems most likely that it is the *less strained grains* (in which the atoms retain their original positions comparatively unchanged) that grow into their *more deformed* neignbours, the disarranged atoms of the latter being compelled to rearray themselves according to the orientation of the former.[1] Possibly the form of the boundary separating the grains may have an influence in determining growth, since there will be a tendency for growth to commence in such a direction as will cause the boundary to "straighten out," thus reducing the interfacial energy of the system.[2]

(*b*) **Recrystallization from new centres** is characteristic of a higher degree of deformation. The new centres appear to be formed spontaneously in the "amorphous" material which exists at the boundary of the distorted grains and elsewhere. When once the crystallites appear at the boundaries, they act as nuclei upon which the disordered atoms of the shattered grains can array themselves, and the process continues until the whole metal is crystallized afresh. The number of nuclei will be greater, the greater amount of amorphous matter present; consequently, a high degree of deformation is likely to give a larger number of crystals in the final state—and consequently, a smaller grain-size—than a comparatively small degree of deformation.

Much information has been derived from a study of the behaviour of rolled aluminium on annealing.[3] The original structure of the rolled metal (Fig. 42A) consists of thin lamellæ, which may perhaps be regarded as the original crystals of the cast metal very much elongated in the direction of rolling. On annealing at about 300° C., new crystals appear in about three hours at the boundaries between these lamellæ; they can fortunately be distinguished from the old crystals as they tarnish less readily, and therefore show up in the micro-sections as white grains on a darker background. Fig. 42B shows three new crystals which have appeared at the grain boundaries. On further annealing, these new crystals spread out until the whole mass is recrystallized; the metal has then acquired something of a polygonal structure, rather similar to that of a cast metal. It should, however, be noticed that even the new crystals are somewhat elongated in the direction of rolling (Fig. 42C). An explanation of this remarkable fact may be suggested. The growth of crystals from the nuclei that arise spontaneously in the boundary will occur more quickly in the direction of rolling than it will do in the direction at right angles. For crystallization in the direction of rolling involves only the rearranging of the utterly disordered atoms which exist along the boundaries of the old elongated grains, whereas growth in the direction at right angles requires the re-arranging of atoms which still retain some vestige of their old orientation—a fact which will undoubtedly militate against their assuming the new system of orientation.

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[1] Prof. Carpenter and Miss Elam originally thought that the strained grains grow into the less strained. It appears, however, at variance with the ordinary ideas of crystallization that the more disarrayed atoms should compel the less disarrayed atoms to rearray themselves according to the vestiges of orientation remaining among the former. See U. R. Evans, *J. Inst. Met.* **25** (1921), 298. Professor Carpenter and Miss Elam deal with the difficulty raised by the present writer in *Proc. Roy. Soc.* **100** [A] (1921), 351. The view of the present writer is supported by C. J. Smithells, *J. Inst. Met.* **27** (1922), 107. Smithells thinks, however, that the relative size of the grains is also an important factor. The present writer thinks it unlikely that size has any direct effect. Carpenter and Elam's experiments certainly seem to indicate that the big grains do not in every case swallow the small ones.

[2] U. R. Evans, *J. Inst. Met.* **27** (1922), 139.

[3] H. C. H. Carpenter and C. F. Elam, *J. Inst. Met.* **25** (1921), 259. Compare E. Rassow and L. Velde, *Zeitsch. Metallkunde*, **12** (1920), 369, who find that in copper also recrystallization commences at the grain boundaries.

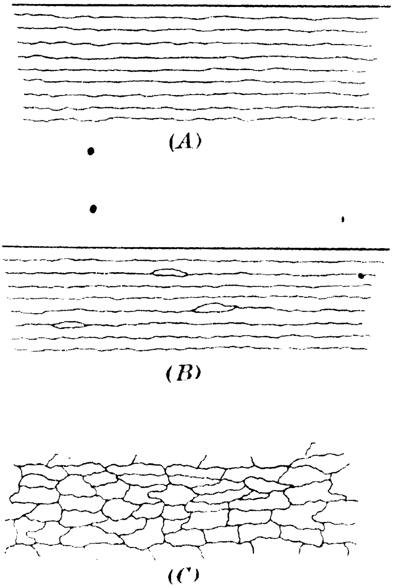

Fig. 42.—Rolled Aluminium: (a) before annealing; (b) annealed 3 hours at 300°; (c) annealed for several weeks.

In several other metals, the grains produced after recrystallization are elongated in a manner related to the direction of previous deformation.[1] But in the annealing of rolled cupro-nickel, where the amorphous material appears to exist mainly along the planes of gliding, the new crystals first appear in the gliding-planes and grow most quickly in the direction of gliding. Thus these new crystals tend to become elongated in the direction of gliding, not in the direction of rolling.[1]

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[1] Compare W. E. Ruder, *Trans. Amer. Inst. Min. Eng.* 47 (1913), 575.

The fact that a low degree of deformation will give rise to a larger grain-size than a high degree of deformation is of some importance in industry, because coarseness of grain is a cause of fragility. In the ordinary articles which have undergone a considerable amount of mechanical working, a good deal of latitude can be allowed in the choice of annealing conditions without fear of brittleness. But where the degree of deformation is small, brittleness may occur unless the annealing conditions are carefully chosen. Wire which has suffered considerable reduction of area by passing through a die rarely becomes coarse on annealing; but wire which has merely undergone a straightening operation—involving only very slight deformation—readily becomes coarsely crystalline when annealed.[2]

Effect of Temperature on Grain-size. The effect of the annealing temperature upon the grain-size produced is also a matter of some importance in industrial work. At a high temperature, a short annealing will cause grain-growth in a piece of metal which has undergone too little deformation to allow of any grain-growth at a lower temperature. In the technical annealing of articles, an unduly high temperature is rightly looked upon as dangerous—being likely to cause a coarse grain-size and consequent fragility. But, in some cases at least, this is due to the fact that the articles in question are deformed to a different extent in different parts; and whilst annealing at a low temperature only causes a change of structure in the highly deformed portions, the annealing at a high temperature will cause growth to occur also in the less deformed parts—with the consequent production of coarse grains. In such a case, it is the small degree of deformation which is the primary cause of coarseness, and the temperature acts merely as a determining factor which decides whether growth can occur in the slightly deformed parts or not.

This is shown very well by the work of Hanson on aluminium.[3] A test piece was cut which was tapered towards the centre, and was strained until it broke at the centre. One half was annealed at 450° C., the other for a longer time at 480° C.; the two halves were etched with hydrofluoric acid, and are represented in Fig. 43, side by side.

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[1] F. Adcock, *J. Inst. Met.* **27** (1922), 73.

[2] H. M. Howe, *Trans. Amer. Inst. Min. Eng.* **56** (1916–17), 585.

[3] D. Hanson, *J. Inst. Met.* **20** (1918), 141.

It is clear that the stress per unit area must have been greater at the narrow portion near the centre than at broad portion near the shoulder. It is not surprising, therefore, to find that, in each piece, the grain is fine at the centre, but becomes coarser as the shoulder is approached. At corresponding levels (and therefore at points of equal deformation) the grain-size is very nearly the same in both pieces; but in the piece annealed at 480° C. the recrystallization has extended to a point much farther down in the region of low strain; consequently a larger size of grain has been reached. Similar results have been obtained with other metals.

As to whether—in a *uniformly stressed* specimen—a high annealing temperature will cause a large grain-size or a small grain-size is another matter, and the answer is different in the case of different metals. In brass [1] and in tin,[2] for instance, a high temperature of annealing has been shown to cause a coarser grain than is produced by annealing at a low temperature, other things being equal. On the other hand in zinc [3] and in aluminium,[4] a high temperature produces growth from many centres, and consequently a finer grain-size, than a low temperature. Two American metallographists, Howe [5] and Jeffries,[6] have laid great emphasis on the production of coarse crystals at the so-called "**germinative temperature**"—that is the *lowest* temperature at which a given piece of deformed metal will show any alteration in structure; it is, of course, lower for highly deformed metal than for slightly deformed metal. They consider that at the germinative temperature, only a few grains (those most favourably situated) will become "germinant" (i.e. will start to grow) and consequently a coarse structure will be produced. Experiments have been described to show that if a metal wire is heated electrically, so that

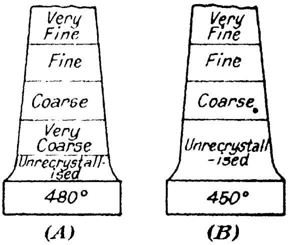

FIG. 43.—Tapered Aluminium Test Bar annealed: (A) at 480° C. for 30 minutes; (B) at 450° C. for 5 minutes.
Based on photograph by Hanson.

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[1] C. H. Mathewson and A. Phillips, *Trans. Amer. Inst. Min. Eng.* **54** (1916), 608.

[2] J. Czochralski, *Int. Zeitsch. Met.* **8** (1916), 1.

[3] G. Masing, *Zeitsch. Metallkunde*, **13** (1921), 425.

[4] H. C. H. Carpenter and C. F. Elam, *Proc. Roy. Soc.* **100** [A] (1921), 329.

[5] H. M. Howe, *Trans. Amer. Inst. Min. Eng.* **56** (1916–17), 571.

[6] Z. Jeffries, *Trans. Amer. Inst. Min. Eng.* **54** (1916), 658; **56** (1916–17), 582; *J. Inst. Met.* **20** (1918), 109.

the central portion is just above the germinative temperature, and the surface of the wire (owing to radiation) is just below it, the "germinant" grains of the hot interior will grow outwards into the "inert" exterior portion, and thus produce a coarse radial structure. In explaining such phenomena, the conception of a "germinative temperature" may be extremely useful; the conception has been applied especially in discussing the important question of the grain-size of tungsten. But many metallographists consider that it has been used to interpret cases which could more conveniently be explained in other ways. If the production of coarse grains at the germinative temperature were a common occurrence, one would expect that, in ordinary annealing practice, the rate of heating up an article through the germinative temperature would be of vital importance. For if the article remained for any appreciable period at the germinative temperature, one would imagine—on the Jeffries-Howe theory—that coarse grains would develop. Actually, however, the rate of heating seems to make little difference.[1] Coarse grains only develop where the final temperature is unduly high, or where the degree of deformation has been abnormally low.

Effect of Duration of Annealing. The time during which annealing is carried on clearly affects the state of the metal after the process; but, if sufficient time is allowed, a stage is always reached in which continued annealing seems to have no further effect. This cannot occur until the various growing grains have met one another at all points, and may not occur even then, since occasionally recrystallization is followed by the growth of the new crystals into one another. Sooner or later, however, a stage is reached at which there is no further change; or at any-rate the further change is so slow as to be capable of being neglected.

The time required to reach this final stage depends very much on the temperature. A very small lowering in the temperature will increase to a most remarkable extent the time required to reach the completely annealed condition. In iron, the time required at different temperatures to reach a corresponding condition (not necessarily the final condition) is shown on the next page.[2]

Effect of Obstructions on Grain-growth. Another very important factor in determining the resistance of a material to an exaggerated grain-growth is the presence of impurities; if the grains of the original material were separated by a network containing a second metal, or an inter-metallic compound or a carbide, the

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[1] Compare A. Phillips and G. C. Gerner, *Met. Chem. Eng.* **20** (1919), 622.

[2] According to A. E. White and H. F. Wood, *Proc. Amer. Soc. Test. Mat.* **16** (1916), 82.

Equivalent Times for Annealing at Different Temperatures.

8 minutes	675°
24 minutes	650°
$3\frac{1}{2}$ hours	600°
$32\frac{1}{2}$ hours	550

growth of each grain—as will be readily understood—is hindered; inclusions of slag within the metal produce a similar effect.[1]

Where the impurities occur in a banded arrangement throughout the metal, as in the case of "pearlitic" steel, the obstruction is naturally most pronounced; and it is not surprising to find that the tendency of iron and low-carbon steel to "coarsen" on annealing falls off rapidly as the carbon-content increases.[2]

The presence in metallic tungsten of certain oxides, such as thoria, lime, and in a lesser degree alumina, has a very marked effect in restraining the grain-growth on annealing; the impurities collect at the grain-boundaries when the metal is annealed, and prevent the growth of one grain into another.[3]

Objects of Annealing. The object aimed at in annealing a metal differs in various cases.

If it is desired[4] to subject metal to considerable change of shape (for instance, to draw out rod into thin wire), the deformation renders the metal hard and brittle; and, if any attempt were made to carry out the process in one step, the metal would certainly fracture before the desired effect was produced. Consequently, after a certain amount of deformation has occurred, the metal is annealed at a fairly high temperature; the annealing removes the effect of cold work, reduces the elastic limit, rendering the metal ductile once more, so that the deformation process can be continued. By alternate annealing and deformation the process can continue until the product is of the desired form.

The annealing of a finished article, has, however, a different object—namely, to remove the internal stresses which have already been referred to (see page **164**). An object which has acquired its shape through cold-work, although to outward appearance stable enough, is internally in a state of stress.[1] In a cold-drawn ba for instance, the outside layer is in a state of tension and the centra portion is in a state of compression, as suggested, fancifully, i Fig. 44. Obviously, since the bar as a whole does not elongate o shrink, the forces balance one another; obviously, also, the stresse are in every part less than the "maximum stress" which th material can withstand. But a very little extra stretching forc may cause the maximum stress of the outer parts to be exceeded and cracking may result, therefore, by the external applicatio to the bar of quite trifling forces. Failure may also arise—especiall in brass—in a different way; a corrosive agent, such as ammonia, which has a selective action upon the inter-granular material, may commence to eat away the metal at the boundaries of the grains. The internal tensional stresses aid the action by pulling apart the grains wherever the inter-granular cement has been removed, thus opening the cracks between the grains and allowing the corrosive agent to penetrate farther. In this way the phenomenon of **season-cracking** referred to in the last chapter may occur.

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[1] Compare the views of G. Tammann, *Zeitsch. Anorg. Chem.* **113** (1920), 175, 176.

[2] C. Chapell, *J. Iron Steel Inst.* **89** (1914), 489–491. H. M. Howe, *Trans. Amer. Inst. Min. Eng.* **56** (1916–17), 586–587. R. H. Sherry, *Trans. Faraday Soc.* **12** (1916–17), 285.

[3] C. J. Smithells, *J. Inst. Met.* 27 (1922), 107.

[4] G. D. Bengough and O. F. Hudson, *J. Inst. Met.* **1** (1909), 89; F. C. Thompson, *Trans. Faraday Soc.* **12** (1917), 30.

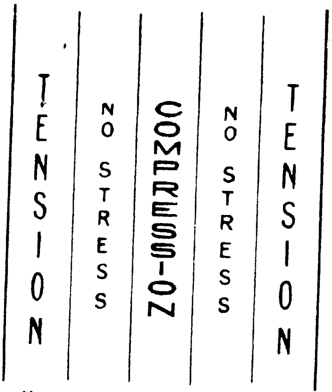

FIG. 44.—Internal Stresses in a Cold-drawn Bar.

Evidently, therefore, the internal stresses due to cold-work must be removed by annealing, before any article can be looked upon as trustworthy. The temperature chosen must be high enough to accomplish this; but an unduly high temperature is to be avoided, since it may lead in some cases to undue coarseness of grain; a high temperature also involves danger of "burning"—that is oxidation of the material, accompanied sometimes by partial vaporization of a volatile constituent, like zinc, from an alloy. Moreover, in some cases, even where there is no burning, an unduly high temperature causes the boundaries between the grains to be straighter and smoother than would otherwise be the case; as has already been explained; this may, long afterwards, lead to intergranular cracking.[1]

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[1] E. Heyn, *J. Inst. Met.* **12** (1914), 3; *Int. Ass. Test. Mat. 6th Congress* (1912), II, p. 45. See also W. H. Hatfield and G. L. Thirkell, *J. Inst. Met.* **22** (1919), 67; W. H. Hatfield, *Trans. Faraday Soc.* **17** (1921), 36; H. Moore and S. Beckinsale, *J. Inst. Met.* **23** (1920), 225; **27** (1922), 149; H. Moore, S. Beckinsale and C. E. Mallinson, *J. Inst. Met.* **25** (1921), 35; R. H. N. Vaudrey and W. E. Ballard, *Trans. Faraday Soc.* **17** (1921), 52.

Finally, it should be pointed out that the annealing of iron and steel may have a third object, namely, to " refine " a coarse structure. This refining is possible in those metals and alloys which undergo allotropic changes at high temperatures; in the case of iron, there is a complete crystallographic rearrangement of the atoms, when it is heated above a certain temperature, which is about 900° C. in pure iron, and rather lower in iron containing carbon. All traces of the structure present at ordinary temperatures can thus be removed, and by cooling from this high temperature, a finer structure may often be obtained than was present before the annealing. Consequently for iron and steel the connection between grain-size and annealing conditions differs considerably from that existing in the majority of metals.

Summary. Any metal, when stressed beyond the " yield-point," suffers permanent deformation. Sometimes this is caused by some portions of the grains sliding over the other portions along " gliding-planes," a gliding-plane being usually a possible cleavage-plane; sometimes, especially in the case of local compressional stresses, deformation occurs by " twinning " ; sometimes again it appears to occur by gradual distortion of the space-lattice as a whole. If stressed beyond the " maximum stress," the metal thins out at a point and fractures. " Ductile " metals are able to suffer considerable elongation before they fracture, ductility being determined by the power to form gliding-planes readily; metals, which cannot accommodate themselves to sudden stresses by gliding, and which therefore fracture readily upon shock, are said to be "brittle." Coarse-grained metal is more likely to fail in this way than fine-grained, and is normally less strong, although, at high temperatures, the fine-grained metal, containing more inter-granular amorphous material, is the weaker of the two.

Mechanical deformation at low temperatures (" cold-work ") alters the properties of metals, usually rendering them stronger, harder, less ductile, less conductive, and more chemically reactive. This is usually ascribed to the formation of more or less amorphous material along the gliding-planes and at the grain-boundaries. The polishing of a metallic surface consists in smearing a varnish of " amorphous " metal over the whole, so as to fill up, or bridge over, any minute depressions, and thus render the surface smooth and glassy.

When the cold-worked metal is annealed, it loses its extra strength and hardness, and regains ductility. In slightly deformed metals, growth of certain of the existing grains takes place. In highly deformed metal, recrystallization starts from fresh centres in the amorphous material at the grain-boundaries or on the gliding-planes; on the assumption that the amorphous (or disordered) metal is equivalent to a glass, this is easily understood. In general the grain-size of the annealed metal will be coarsest where the deformation has been least—assuming always that the temperature is sufficiently high and the time allowed sufficiently long for the recrystallization from the nuclei to take place at all. In an unequally strained piece of metal, the occurrence of a zone of large crystals at the border between the unchanged and recrystallized portions is to be expected.

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[1] W. Rosenhain, *J. Inst. Met.* **22** (1919), **93**, 9

Cold-worked articles, if not annealed, retain internal stresses which may cause unexpected failure when the articles have been in use for some time.

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CHAPTER III

PYROMETRY AND COOLING CURVES

Whilst much direct information regarding the structure of metals and alloys is obtained from the study of micro-sections, an equally valuable—if less direct—method of investigation has still to be described. It is based upon variations in the speed at which the temperature falls when a piece of hot metal is allowed to radiate away heat at a uniform rate. In the case of simple metals, the method is used mainly for the determination of the melting-point, although it occasionally gives information regarding changes which occur in the solid state; but when we turn to the study of alloys, we shall find that the information provided by the "**cooling-curve**" method—as it is called—is, in many cases, the foundation of most of our exact knowledge regarding the constitution of the materials under consideration.

The Thermo-electric Pyrometer. The first necessity is clearly some form of temperature measurer, or "**pyrometer,**" which can be used at high ranges over which the mercury thermometer is not available. The simplest and most convenient form of pyrometer is the thermo-couple, the principle of which has already been explained in the introduction (page 15). The essential part of a couple consists of two wires of different metals welded or twisted together at the ends. For accurate work, one should be of platinum, and the other an alloy of platinum with 10 per cent. of rhodium. Where a very high degree of accuracy is not needed, it is generally unnecessary to employ these expensive materials, since base-metal couples give quite good results, so long as they are not used at too high a temperature.[1] The following pairs of metals have been recommended by different authorities and are in some cases used in commercially prepared thermo-couples.

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[1] See C. R. Darling, *Trans. Faraday Soc.* **13** (1918), 344; O. L. Kowalke, *Trans. Amer. Electrochem. Soc.* **24** (1913), 377; W. Rosenhain, "Introduction to Physical Metallurgy" (Constable) (1914 edition), p. 80.

Nickel :	Nickel-chromium alloy.
Nickel containing a little iron :	Iron containing a little nickel.
Nickel containing a little aluminium :	Nickel containing a little iron.
Iron :	"Constantan" (60 per cent. copper, 40 per cent. chromium).
Copper :	"Constantan."

For use at very high temperatures, a tungsten-molybdenum couple has been advocated.[1]

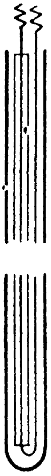

FIG. 45.

Whichever pair of metals is chosen, the two wires are welded together, or tightly twisted together, at their ends, and a thin sleeve, consisting of a quartz tube, is slipped over one wire to prevent them from coming into contact at other points (Fig. 45). The two wires are then surrounded by an outer tube of quartz or fire-clay. The outer tube must be stout enough to withstand any hard usage which it may receive; but for "cooling-curve" work in the laboratory, it should not be made unnecessarily thick, since any considerable addition to the thickness involves a difference between the temperature of the metallic junction and that of the metal specimen whose temperature it is desired to measure.

For the same reason the pyrometer must be placed in close contact with the specimen; if a solid metal is to be examined, a hole should be bored, if possible, in it, and the end of the pyrometer tube inserted (J_1) (Fig. 46). The upper ends of the two wires, M_1 and M_2, carefully kept apart from each other, pass to the cold junction, or more correctly the cold junctions (J_2 and J_3), where each of them is brought into contact with a copper wire; the two copper wires (C_1 and C_2) pass on to a high resistance milli-voltmeter. The cold junctions are usually maintained at a constant temperature by being placed in a water bath, kept at 15° or at 0° C.

In the arrangement just described there are really three junctions, namely :—

(Hot) Junction, J_1, in the pyrometer, between the two chosen metals M_1 and M_2.
(Cold) Junction, J_2 between M_1 and the copper wire C_1.
(Cold) Junction, J_3, between M_2 and the copper wire C_2.

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[1] E. F. Northrup, *Met. Chem. Eng.* **11** (1913), 45. See, however, discussion on pages 66–67.

It will be obvious that if all the three junctions J_1, J_2 and J_3 are at the same temperature, no current can be produced; the algebraic sum of the three P.D.s is evidently zero. If, however, J_1 is hotter than J_2 and J_3, the P.D.s no longer balance one another, and the E.M.F. produced is indicated by the milli-voltmeter (G), the deflection of which will serve to measure the temperature of J_1.

The instrument may be calibrated by placing the pyrometer in various baths the temperature of which is known. A good way of carrying out the calibration is to immerse the pyrometer in a molten metal the melting-point of which is known; the metal is allowed to cool, and the deflection is noted whilst the metal is solidifying. The same operation is carried out for various other metals of known melting-point, and a curve showing the connection between the temperatures and the reading of the milli-voltmeter can then be plotted.

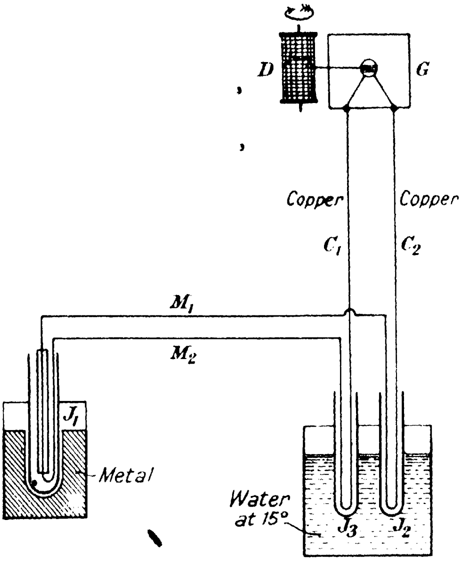

FIG. 46.—Connections of Thermo-electric Pyrometer.

In taking a cooling-curve it is sometimes possible to use a self-recording milli-voltmeter [1]; in modern types of recording instruments, a stylus attached to the moving coil makes a trace upon a chart mounted on a slowly revolving drum (D). The trace will afterwards constitute a diagram showing the variation of temperature with time. Unfortunately the E.M.F. provided by the thermo-couple is not sufficient to drag an ordinary ink stylus across the paper, if the stylus is kept constantly in contact with the latter. The moving coil, therefore, is provided with a stylus, which normally swings just clear of the surface of the paper, and is therefore able to take up its position without being impeded by friction. The apparatus, however, is provided with a bar (generally actuated by the same clockwork as turns the drum) which periodically presses the stylus on to the paper, thus making a dot. The series of dots produced on the chart blend to form a curve showing the relations between time and temperature.

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[1] See C. R. Darling, *Trans. Faraday Soc.* **10** (1914), 139; G. K. Burgess, *Electrochem. Ind.* **6** (1908), 366.

The method of measuring the E.M.F. generated by a thermo-couple directly by means of a milli-voltmeter is not wholly free from objection. Unless the resistance of the instrument is very high, an uncertain part of the P.D. will fall over the wires of the thermo-couple and the connecting leads. Furthermore if the scale of the milli-voltmeter has to represent a range of temperatures from 0° C. up to, say, 1200° C., it will clearly be impossible to read temperatures with a great degree of accuracy. For accurate reading various elaborations have been introduced.[1] If the E.M.F. provided by the thermo-couple is opposed by a slightly smaller E.M.F. of known magnitude which remains fixed during the measurements, the small residual E.M.F. of the combination can be measured on a milli-voltmeter of greater sensitiveness; the scale of this sensitive milli-voltmeter now represents a limited range of temperature only (e.g. 1,100° to 1,200° C.) and the temperature can be read with greater accuracy. The known E.M.F. needed to balance the greater part of the E.M.F. of the thermo-couple is only a fraction of a volt; it could be provided by inserting a specially designed standard cell in the circuit between the thermo-couple and the milli-voltmeter, but in practice it is more conveniently provided by means of the instrument known as the "potentiometer," which will be described in Chapter VIII.

It is possible to measure the E.M.F. provided by the thermo-couple by means of the "potentiometer" alone, no milli-voltmeter being employed, according to the method of "balance" described in Chapter VIII. This method, although very accurate, is inconveniently slow for use when a quickly cooling specimen is being tested.

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[1] A. Stansfield, *Phil. Mag.* **46** (1898), 59; N. S. Kurnakow, *Zeitsch. Anorg. Chem.* **42** (1904), 184; H. C. H. Carpenter and B. F. E. Keeling, *J. Iron Steel Inst.* **65** (1904), 226; W. P. White, *Phys. Rev.* **25** (1907), 334.

The Resistance Pyrometer. Other forms of pyrometers, based upon principles different from that of the thermo-couple, have been designed. One of these is based upon the variation of the resistance of platinum with the temperature. A recording instrument working upon this principle has been designed for giving a continuous chart of the variations of temperature with time, and has been used for some of the best researches upon the structure of alloys.[1] It is, however, rather more complicated than the thermo-electric pyrometer.

Furnace for Cooling Curves. The type of furnace suitable for the preparation of cooling curves must fulfil two conditions. Firstly, it must be capable of heating the specimen to the highest temperature required, and secondly, it must allow the specimen to cool at a moderately constant rate. Properly designed gas-fired furnaces can be made to yield good results if the range of temperature required is not too high. But electrically heated furnaces are more suitable for the work, and a form recently designed at the National Physical Laboratory[2] may be referred to specially, because it is probably the type of furnace which best fulfils the required conditions. The furnace (Fig. 47) consists of a vertical fireclay tube about 2 ft. 6 in. long; at the top end only, nickel-chromium wire is wound round it for a length of about 6 inches. The outside of the whole is then surrounded by a heat-insulating material, preferably magnesia, to reduce the rate at which heat is radiated away; the lower end is surrounded by a water jacket.

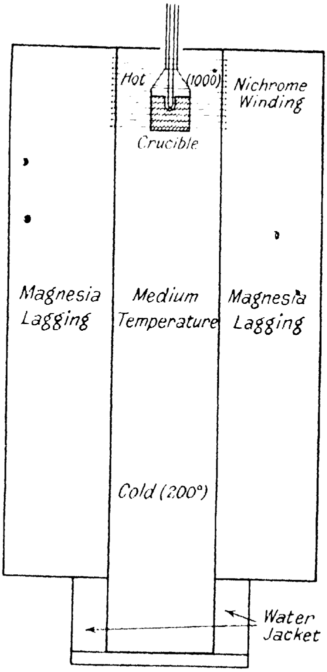

FIG. 47.—Electric Furnace designed to give even Temperature Gradient.

When a strong current of electricity is passed through the nickel-chromium wire, the wire becomes intensely hot. The temperature of the furnace at the upper (hot) end reaches about 1,000°, whilst that of the lower (cold) end is below 200°, the central part of the furnace being of course at intermediate temperatures. The specimen to be tested is placed, together with the thermo-couple, in a small crucible which is suspended by wire, and which can be lowered to any point in the furnace according to the temperature desired. The specimen has first to be heated, for which purpose it is kept at the hot end. When the necessary temperature is reached, it is lowered so as to allow cooling to commence. If it is desired that the cooling shall be rapid, it is lowered far into the furnace; if slow cooling is aimed at, it is kept at a comparatively high level. Thus any desired rate of cooling can be obtained at will. If, however, the specimen is kept at the same place throughout the period of cooling, the rate will not be uniform; for the specimen whilst very hot will loose heat quickly, but, as it comes to a temperature nearer to that of the walls immediately around it, it will radiate away heat at a lower rate. To obtain uniform cooling, therefore, arrangements are made for the crucible to be gradually lowered, as it cools, at a constant speed, towards the colder end. This refinement adds somewhat to the complexity of the apparatus, but even without it the furnace would be of great value for the obtaining of cooling curves.[1]

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[1] C. T. Heycock and F. H. Neville, *Trans. Chem. Soc.* 67 (1895), 160.
[2] W. Rosenhain, *J. Inst. Met.* 13 (1915), 164.

Comparison of Cooling Curves. The trace made by the recording milli-voltmeter as the metal specimen cools shows the variation of temperature with time, and constitutes a cooling-curve; if a recording instrument is not used, the observer takes readings of the temperature at intervals during the cooling and plots the temperature against the time. Assuming the rate of cooling has been perfectly uniform, the trace will be a straight line, as shown in curve A (Fig. 48); but, unless the special device mentioned above is available, the cooling will usually become slower as the temperature drops, causing the trace to be slightly concave, as is shown in curve B.

Supposing, now, that we start with a metal in the molten condition (curve C). As it loses heat the temperature drops normally until the freezing-point is reached, and solid begins to appear. The process of crystallization of the metal causes an evolution of heat, and thus for a time supplies as much heat as is lost by radiation. As long as any liquid remains, the temperature must remain at the melting-point, which is, of course, the only temperature at which solid and liquid can co-exist. When all the metal has solidified, however, the temperature commences to drop again.

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[1] Another device for obtaining a constant rate of heat-removal is described by W. Plato, *Zeitsch. Phys. Chem.* **55** (1906), 721.

It is evident that, during a change such as freezing, an "arrest" in the cooling will occur, and that by observing where this arrest occurs on the curve, the melting-point may be determined. It should, however, be noticed that the metal is often cooled down some little way below the melting-point before solidification commences; this phenomenon of "super-cooling," which has been mentioned in the first chapter, is most marked when the rate of cooling is rapid, as in curve D. As soon as freezing begins, however, the temperature rises at once to the true melting-point, owing to the evolution of heat due to solidification, and remains there until practically all the liquid has disappeared.

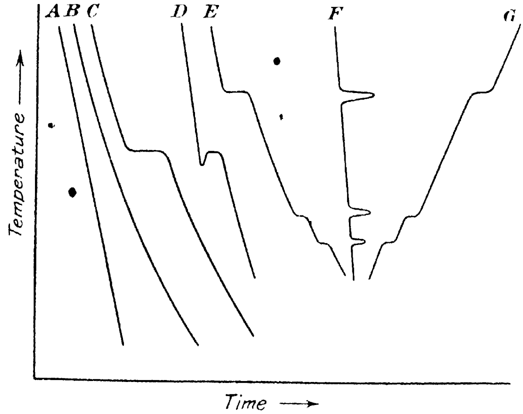

Fig. 48.

Sometimes the cooling-curve indicates other transformations taking place in the solid metal at temperatures below the melting-point. Curve E is a diagrammatic representation of a cooling-curve of pure iron, and shows three arrests. The highest of them (at 1,530° C.) corresponds to the melting-point of iron; the others (at about 889° and 768°) indicate some change in the solid state.[1] It is considered that the iron at temperatures above 889° exists in a modification known as γ-iron, which is crystallographically different from the modification, α-iron, which we know at ordinary temperatures. α- and γ-iron are said to be "allotropic modifications" of iron, or simply "**allotropes**"; in α-iron the atoms are arranged on a centred cubic space-lattice, whilst in γ-iron they are arranged on a face-centred cubic lattice.[1]

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[1] The values here quoted are taken from a paper by G. K. Burgess and J. J. Crowe, *Trans. Amer. Inst. Min. Eng.* **47** (1913), 665, and refer to values actually obtained on a cooling-curve; they do not represent the equilibrium transformation points.

The evolution of heat which causes the arrest at about 889° is believed to be due to the "allotropic change" (the conversion of γ-iron into α-iron), which is evidently an exothermic process. The arrest at 768° is of a different character, and is thought to be due to the acquisition of ferro-magnetic properties which is known to take place at that temperature. The change differs in many ways from that at 889°, and is not generally regarded as an allotropic change. The matter will be discussed more fully in the section upon iron (Vol. III), but it may at once be stated that those who regard the change at 768° as allotropic, apply the name β-iron to the variety which exists between 768° and 889°, retaining that of α-iron for the magnetic form which exists from 768° down to ordinary temperatures.

Other Modes of Expression of Cooling Curves. Unless the milli-voltmeter attached to the pyrometer is a self-recording instrument, the deflection is recorded by the observer at regular intervals of time during the cooling. From the observations recorded it is easy to plot a cooling curve of the type represented by curve E showing the relation of temperature to time. It is perhaps rather more effective to use the same data to plot an "inverse-rate curve," like curve F, which shows the arrests more clearly. In an "inverse-rate curve," the ordinates represent the temperature, and the abscissæ indicate the time taken to fall from that temperature to a temperature 1° C. below it; the arrest points are, of course, indicated by the sharp apices pointing towards the right.

"Differential" Method of detecting Transformations in Solid Bodies. One useful method of detecting a transformation in a cooling metal, which is practically independent of "chance variations" in the rate of loss of heat caused by external influences, is known as the differential method. The metal specimen under examination is placed in the furnace, and close to it is placed a specimen of some standard material which is known to undergo no transformations within the range of temperature in question; nickel and platinum have both been used for this purpose. In addition to the thermo-couple designed to measure the temperature of the specimen under examination, two other thermo-couples joined in series are inserted in the two specimens and are connected to a separate milli-voltmeter so as to indicate the *difference of temperature* between the specimen under examination and the standard material. If the size of the standard has been correctly chosen, the two specimens should cool approximately at the same rate, and the difference of temperature will be very small. But when the temperature corresponding to an exothermic change in the first specimen is reached, the temperature of that specimen ceases to fall; since the temperature of the standard material continues to fall, the difference of temperature between the two suddenly becomes considerable, and the sudden increase in the reading of the milli-voltmeter indicates very clearly that a transformation in the specimen is taking place.[1] However, in view of the recent improvements in furnace design, which render the rate of loss of heat of cooling specimens practically independent of external influences, the differential method is likely to become less important in the future than it has been in the past.

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[1] A. Westgren, *J. Iron Steel Inst.* **103** (1921), 303.

Heating Curves. If, instead of allowing the specimen to cool down steadily, we commence with the specimen cold and supply it with heat at a uniform rate, noting the rise of temperature with the time, a "heating curve" is produced. If properly obtained a heating curve gives as much information as a cooling curve. With a crude furnace it is difficult to ensure that heat is added at a steady rate; but, with the form of electric furnace described above, there is no reason why perfect confidence should not be placed upon the heating curve obtained.[2]

When a substance is heated, the various transformations which were noted on cooling occur again, but in the opposite direction and usually at a rather higher temperature. When pure iron is heated, for instance, it first of all loses its ferro-magnetism at about 768° C., then becomes converted to the allotrope γ-iron somewhat above 909°, and finally melts at 1,530°; each of these changes is shown by an arrest on the heating curve (curve G). Since the temperatures at which the various arrests occur on heating are not always the same as those at which they occur on cooling, it is necessary to distinguish between the "arrest on cooling," represented by the letters Ar ("*Arrêt refroidissement*") and the "arrest on heating," represented by the letters Ac ("*Arrêt chauffage*"). In the case of iron, the exact temperatures of the arrests corresponding to the disappearance and reappearance of γ-iron are written Ar_3 and Ac_3, whilst those corresponding to the appearance and disappearance of ferro-magnetism, are written Ar_2 and Ac_2. At ordinary rates of heating or cooling Ac_2 and Ar_2 are quite close together, and, at an "infinitely slow" rate of heating, the change appears to occur at a temperature independent of the direction of the transformation. Thus

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[1] For further developments of this method, see S. L. Hoyt, "Metallography" (McGraw-Hill), Vol. I, pages 154–158 (1920 edition).

[2] For comparison between cooling curves and heating curves, see L. I. Dana and P. D. Foote, *Trans. Faraday Soc.* **15** (1920), iii. 189.

$$Ar_2 = Ac_2 = 768° C.$$

On the other hand, the temperature of the A_3 change invariably depends greatly on the direction in which it is proceeding. Ac_3 generally lies well above Ar_3, although by using very pure iron (free from carbon and from occluded gases) and by employing a very low rate of heating and cooling, Ac_3 and Ar_3 can be brought close together. But, even if the rate of alteration of temperature is made extremely small, and all factors which could cause the transformation to "lag" are removed, Ac_3 still lies about 11° above Ar_3. The values [1] calculated for pure iron at an "infinitely slow rate" of heating or cooling, are

$$Ac_3 = 909° ; \quad Ar_3 = 898°.$$

Summary. A "cooling curve," showing the connection between temperature and time in a metal which is radiating away heat at constant rate, gives valuable information regarding melting-point and allotropic changes; an arrest observed at any temperature indicates an exothermic change occurring at that point. The temperature is generally measured with a thermo-couple, base-metal couples being now considered reliable for low temperatures. The furnace should be designed in such a way as to render the rate of loss of heat as uniform as possible. In a reliable furnace, "heating curves" showing the relation between time and temperature during the heating up of a specimen give equally valuable information.

The cooling curve of iron shows three "arrests": the highest indicates the solidification, the second (Ar_3) the disappearance of γ-iron, and the lowest (Ar_2) the appearance of ferro-magnetism. The heating curve of iron, shows similar arrests in the opposite order; but whilst the arrest Ac_2 indicating the loss of magnetism occurs at the same temperature as Ar_2, the arrest Ar_3, indicating the return of γ-iron, occurs at a point well above Ar_3. However; in pure iron, Ac_3 and Ar_3 approach one another when the rate of heating and cooling is made very small.

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[1] According to G. K. Burgess and J. J. Crowe, *Trans. Amer. Inst. Min. Eng.* **47** (1913), 665.

CHAPTER IV

THE STRUCTURE OF ALLOYS

Classes of Alloys. When two molten metals are brought together in a vessel, they may form two immiscible layers—as in the case of lead and zinc—or they may mix together to form a single homogeneous liquid. The latter state of affairs is, however, most common, and for the purpose of this chapter, most important; for it is usually by the cooling down of a homogeneous liquid containing more than one metal that a solid "**alloy**" is produced. In order to simplify the treatment of the subject, only alloys containing two metals ("binary alloys") will be considered at present.

It does not follow that because the fluid mixture is homogeneous, the alloy produced will also be homogeneous. For most pairs of metals—whilst completely miscible in the liquid state—will not be completely miscible in the crystalline state. It is convenient to consider separately the classes of alloys produced when the metals are:—

(1) completely *immiscible* in the crystalline state,
(2) completely *miscible*, forming a range of *mixed crystals* of all possible compositions,
(3) *partially miscible*, forming mixed crystals within certain limits of composition.

Two more possibilities must be added, in which

(4) one or more *inter-metallic compounds* of *definite* composition are produced,

and (5) *inter-metallic compounds* are formed which are capable of holding *excess of one or both constituent metals in solid solution*.

The terms "solid solution" and "mixed crystal" have come to be synonymous; some metallographers use one term, and some the other. In alloys of Class 5, where our knowledge of the crystal-structure is very scanty, the vaguer term "solid solution" is perhaps preferable.

The first class, although in many ways the simplest, is comparatively rarely met with. Generally the metals are capable of crystallizing together either as mixed crystals (Classes 2 and 3) or intermetallic compounds (Classes 4 and 5).

If the two metals forming the alloy are alike, mixed crystals[1] are usually produced in which the two metals play the same *rôle* in the crystal-structure. For instance, the "transition metals" of the periodic classification, and the metals of the Groups VIIA and IB on either side, possess many properties in common. The salts of these metals are frequently isomorphous; that is to say, the atom of one metal can replace that of another in the crystal structure of the salt. It is not surprising that the same power applies to the crystal-structure of the elements themselves. Silver and gold, which fall in the same group of the periodic table, can form a complete series of mixed crystals, ranging from pure silver to pure gold; silver-gold alloys are assigned therefore to Class 2. Evidently, the atoms of the two metals play the same part in the crystal-structure.

However, complete miscibility in the crystalline state is not always met with. Copper and silver belong to the same group of the periodic table; they both form crystals in which the atoms are arranged on a face-centred cubic lattice. Nevertheless, although, in crystalline silver, a certain number of silver atoms can be replaced by atoms of copper, yet the miscibility in the solid state ceases when the mixed crystals contain about 6 per cent. of copper.[2] Silver-copper alloys are therefore assigned to Class 3.

Whilst a pair of like metals generally form mixed crystals in which both play the *same part* in the crystal-structure, *a pair of metals which are dissimilar in character not infrequently combine together to form an inter-metallic compound* in which each element plays a *distinct rôle* in the crystal-structure. Inter-metallic compounds are rarely—if ever—formed between two metals belonging to the same group of the periodic table (as arranged in this book). In many cases, the compound formed possesses a constant composition which can be expressed by a simple atomic formula, such as Mg_2Pb; the existence of crystals containing both lead and magnesium is only possible if the component atoms are present in the definite ratio (1 : 2) indicated by the formula, and alloys of lead and magnesium are therefore assigned to Class 4.

In other cases, the composition of the crystals containing two metals can vary within certain limits, the series of crystals produced having, therefore, much in common with the "mixed crystals" of Class 3. For instance, in the alloys of gold and magnesium there is one series of mixed crystals which may contain magnesium atoms and gold atoms in any ratio between 1 : 1·8 and 1 : 0·7; many of the properties of the crystals vary continuously as the composition alters. But it is found that the melting-point of the mixed crystals is a maximum when the magnesium and gold atoms are present in equal numbers. This fact suggests that crystals having the composition corresponding to the simple formula AuMg possess a maximum stability—since they can withstand the highest temperature without melting. It is therefore rational to regard the crystals of lower melting-points which contain more gold or more magnesium than corresponds to that simple formula, as less pure forms of the same compound; they can be described as mixed crystals of the compound AuMg and one of the component metals. Such cases are referred to Class 5. There are, however, many series of composite crystals known which it is difficult to regard as being derived from any definite compound and, in view of the uncertainty of the position, it is convenient to speak of these crystals vaguely as "solid solutions," no opinion being expressed regarding the nature either of the solvent or of the solute.

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[1] The factors which determine the formation of mixed crystals and of solid solutions are discussed by N. S. Kurnakow and S. F. Žemežnežny, *Zeitsch. Anorg. Chem.* **54** (1907), 149. See also I. Langmuir, *J. Amer. Chem. Soc.* **38** (1916), 2242.

[2] A possible cause of limited solubility is suggested by W. Rosenhain, *Proc. Roy. Soc.* **99** [A] (1921), 198, 199.

A few examples of well authenticated inter-metallic compounds are given below[1]:

Mg_2Cu	Zn_3Cu_2	Cd_3Cu_4	Al_2Cu $AlCu$ $AlCu_3$		
Mg_3Ag $MgAg$	Zn_3Ag_2	Cd_3Ag_2	$AlAg_2$ $AlAg_3$		
Mg_3Au Mg_2Au $MgAu$		Cd_3Au	Al_2Au $AlAu_2$		
Mg_2Pb					
Mg_2Sn					
Mg_3Bi_2				$NiBi$	Tl_3Bi
Mg_3Sb_2	Zn_3Sb_2 $ZnSb$	Cd_3Sb_2 $CdSb$		$NiSb$	Tl_3Sb

It will be noticed that these formulæ bear no relation to the valencies of the component elements, except where one of the components happens to be arsenic, antimony or bismuth ; in such cases the compounds must be regarded as arsenides, antimonides or bismuthides, and the three elements mentioned really play the parts of non-metals. The failure of the laws of valency in most inter-metallic compounds has already been referred to in the introduction (page 31), and it is only necessary here to restate the opinion there expressed that the existence of this kind of body apparently depends on considerations of geometry rather than of dynamics.

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[1] Taken from M. Guia and C. Guia-Lollini, "Chemical Combination among Metals," translated by G. W. Robinson (Churchill); and from C. H. Desch, "Inter-metallic Compounds" (Longmans, Green & Co.).

It is now possible to study rather more closely a few simple examples of each of the five classes that have been enumerated. It must not be thought that every system of binary alloys can be referred definitely to one or other of these five classes, for in many cases there is some special feature which renders the system slightly different from the simple examples here chosen. If, however, these simple cases are understood, the consideration of any more complicated type of alloy which may be met with hereafter will present no great difficulty.

Class 1. The metals are completely immiscible in the solid state, no mixed crystals being possible.

An example is provided by the alloys of **Gold and Thallium.**[1]

The melting-point of pure thallium is 302° C. ; that is to say pure solid thallium is in equilibrium with pure liquid thallium at 302°. If, however, the liquid is not pure thallium, but thallium diluted with gold, the melting-point is lowered by an amount depending on the concentration of gold ; the equilibrium temperatures of solid thallium in contact with liquid thallium containing various amounts of gold is shown by the curve AP (Fig. 49).

Similarly, pure gold melts at 1,063°, but the melting-point is lowered by the presence of thallium in the liquid phase, as is shown by the curve BP. The two curves cut at 131°, which is evidently the lowest temperature at which a liquid mixture of gold and thallium is stable. This temperature of lowest melting-point is called the **eutectic temperature,** and the composition of the mixture corresponding to it (27 per cent. gold, 73 per cent. thallium) is called the **eutectic composition.**

Consider now what will happen if a molten mixture containing, say, 90 per cent. thallium and 10 per cent. gold is gradually cooled. When the temperature drops to 230°, the curve AP is cut (at the point K) and—assuming there is no super-cooling—the crystallization of thallium will commence. But the separation of the first particles of pure solid thallium leaves the liquid richer in gold, and therefore the temperature must fall farther before crystallization can continue. As the thallium crystal-growths extend, therefore, the temperature continues to fall, the connection between the temperature and the composition of the portion which is still liquid being shown by the curve KP. At the eutectic point, corresponding to a temperature of 131°, the melting-point curve of gold is also cut, and any further cooling would make the liquid super-cooled both to gold and thallium. At this temperature, therefore, gold and thallium solidify simultaneously to form a “ **eutectic mixture** ” (often called simply, a “ **eutectic** ”).

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[1] M. Levin, *Zeitsch. Anorg. Chem.* **45** (1905), 31.

Similarly a liquid mixture containing, say, 20 per cent. thallium,

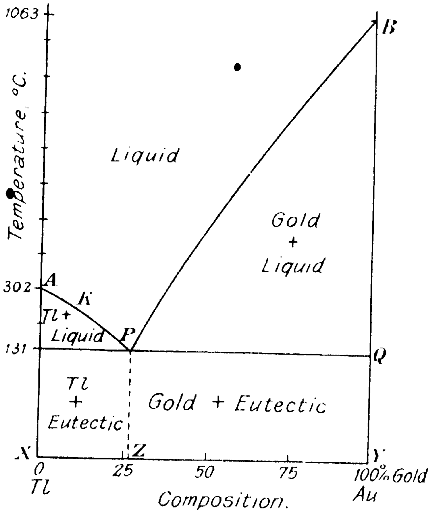

FIG. 49.—The System Gold-thallium.

per cent. gold, will commence to deposit gold at the temperature 5°, and the temperature will continue to fall as the bath becomes her in thallium, until at last, at the eutectic temperature 131°, ld and thallium are deposited together.

If sections of the solidified alloys of different compositions be epared, the structure will be found to support the description the solidification process just given. The solid alloy containing per cent. thallium is found to consist of grey masses of pure allium embedded in a heterogeneous ground-mass which is the tectic; the eutectic, actually an intimate mixture of gold and allium, has a golden hue, and appears all the more bright by contrast with the grey grains of pure thallium. On the other hand, alloys containing 80 per cent. gold consist of large primary yellow crystals of gold embedded in the eutectic, which, in this case, appears bluish-green in colour by contrast with the large gold crystals; if, however, the eutectic is examined with a moderately high power microscope, small particles of glittering gold can easily be made out within it.

Since all thallium-gold alloys consist essentially of a conglomerate of pure gold and pure thallium, the colour of the alloys, as viewed by the naked eye, varies gradually with the composition, ranging from the brilliant yellow of the gold-rich alloys to the dull grey of those rich in thallium.

If a liquid mixture having a composition close to that of the eutectic mixture (27 per cent. gold) is prepared, and is cooled down, the alloy formed will consist almost entirely of the eutectic, the structure of which may vary somewhat from place to place according as the separation of gold or thallium happens to commence in any particular region an instant sooner than that of the other constituent. If there were no super-cooling, the two constituents should commence to crystallize simultaneously from different points. In practice, however, one constituent may commence to solidify a moment before the other, in which case the first solidified constituent may appear as a minute crystalline or dendritic growth embedded in the second constituent. For instance, we often find grains of gold surrounded by a ring of thallium, whilst in other places the thallium appears as the first crystallizing constituent.

Eutectic mixtures occur in many alloys, and vary considerably in character. In some eutectics, the two constituents appear to solidify alternately, forming wavy, parallel lamellæ; this laminated structure is particularly characteristic of pearlite, the "eutectoid" constituent of steel, which differs only from a true eutectic in being formed after the whole steel has become solid. An example of the structure of a true eutectic is shown in plate D of the frontispiece.

When a eutectic alloy is heated above the eutectic temperature, it melts once more to form the homogeneous liquid mixture. The formation of this liquid far below the melting-point of either metal is very striking, and indicates that each component of the complex acts, as it were, as a "flux" for the other. Eutectic mixtures are thus useful as easily fusible materials.

Our knowledge of the equilibrium diagram of a system such as thallium-gold is actually based upon the study of the cooling-curves obtained when mixtures of various composition are prepared in the molten state and are allowed to solidify slowly. A distinct slackening in the rate at which the temperature falls indicates clearly the temperature at which solidification begins, and from the results obtained with alloys of different compositions, it is possible to plot the freezing-point curves AP and BP. The cooling-curve of pure thallium (see Fig. 50) shows one long arrest at 302° C. That of the alloy containing 10 per cent. gold shows a diminished rate of cooling at the point where solidification commences, but the temperature continues to drop until the eutectic point is reached; at the eutectic temperature a definite arrest occurs. An alloy with 20 per cent. gold gives a yet longer arrest at the eutectic point, whilst an alloy of the exact eutectic composition (27 per cent.) shows naturally a longer arrest still, since the solidification of the whole alloy occurs at that temperature. If, however, the gold content is still further increased, the arrest at the eutectic point becomes shorter, until in the cooling-curve of pure gold, the only arrest occurs at 1,063°, all trace of the arrest at 131° having naturally vanished.[1]

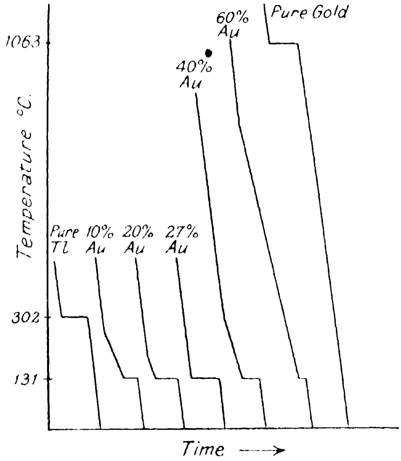

Fig. 50.—Cooling Curves of Gold-thallium Alloys (somewhat diagrammatic).

The duration of the arrest at the eutectic point, commonly known as the "**eutectic time,**" is frequently used by metallographists to find the exact composition corresponding to the eutectic point, the method being due to Tammann. The nearer an alloy is to the eutectic composition, the longer is the halt on the cooling-curve at the eutectic temperature. If the eutectic times of a number of different alloys be plotted against the composition, two lines (AP and BP) are obtained (Fig. 51) which, if produced, will cut one another at a point P; the composition corresponding to P clearly indicates the exact eutectic composition.

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[1] Compare G. Tammann, *Zeitsch. Anorg. Chem.* 37 (1903), 303.

The various lines of the equilibrium diagram (Fig. 49) divide the diagram into areas, each of which is marked in such a way as to indicate the components of the material existing under the conditions represented by points in that area. For example, in Fig. 49 the area PQYZ is marked "gold + eutectic"; these three words, assigned to the area in question, embody a piece of information, which has already been given in the text, namely that, at temperatures below 131°, all alloys containing between 27 per cent. and 100 per cent. gold consists of crystals of gold embedded in the eutectic mixture. Subsequent diagrams will be marked in the same way, and should be studied for information of this kind, which will not in every case be repeated in the text.

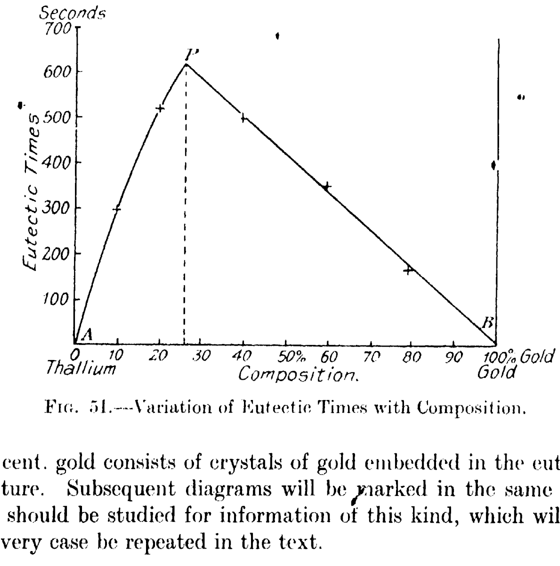

FIG. 51.—Variation of Eutectic Times with Composition.

Class 2. The metals are completely miscible in the solid state. Mixed crystals of all possible compositions are met with.

An example is supplied by the alloys of **nickel and copper.**[1] (Fig. 52).

Pure nickel melts at 1,452°; accordingly molten nickel can deposit solid nickel when cooled below this temperature. The deposition point is, however, lowered by the presence of copper in the fused metal, as is shown by the curve ABC. Thus a molten nickel-copper mixture with 89 per cent. nickel will not commence to crystallize unless cooled to 1,411° C. At that point, separation commences, but the solid deposited is not in this case pure nickel but consists of a mixed crystal containing about 91 per cent. nickel, 9 per cent. copper. The curve ADC shows the composition of the solid substance which is in equilibrium at any particular temperature with the liquid mixture represented by the corresponding

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[1] N. S. Kurnakow and S. F. Żemczużny, *Zeitsch. Anorg. Chem.* **54** (1907), 149. See also W. Guertler and G. Tammann, *Zeitsch. Anorg. Chem.* **52** (1907), 25.

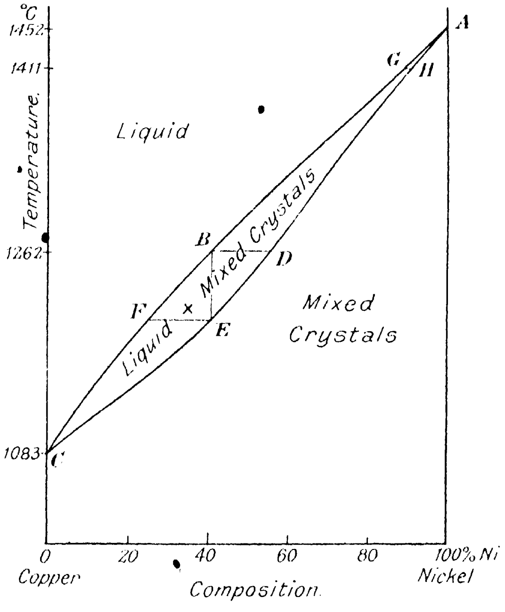

FIG. 52.—The System Nickel Copper.

point on the curve ABC; the curve ADC is known as the "solidus," and ABC as the "liquidus." Thus a liquid mixture with 89 per cent. nickel (point G) commences at 1,411° C. to deposit a solid with 91 per cent. nickel (point H), whilst a liquid with 40 per cent. nickel (point B) begins at 1,262° C. to deposit a solid with 55 per cent. nickel (point D). It will be observed that the addition of nickel to molten copper raises the temperature at which solidification commences; but this is not a real exception to the general rule that the freezing-point of a substance is lowered by the addition of a second substance, because molten copper containing nickel does not deposit pure copper, but always a mixed crystal containing nickel.

Consider now what will happen when a molten mixture containing 40 per cent. nickel, 60 per cent. copper is cooled slowly. At 1,262° C. (point B) solidification will commence, nuclei of an alloy with 55 per cent. nickel (point D) being deposited. This deposition leaves the liquid richer in copper, and thus, as the temperature falls and solidification continues, the composition of the liquid changes in the way shown by the curve BF, whilst the composition of the solid being deposited changes in the way shown by the curve DE. If the cooling is sufficiently slow, the first deposited crystals, which had originally the composition represented by the point D, will gradually absorb more copper, so that when the liquid has reached the composition F—the solid separated will have the composition E. This is the same composition as that of the original liquid (B), and it follows that by the time the whole of the solid has come to have the composition E, the whole of the alloy must have passed into the solid condition. In fact, the "solidus" curve can be defined as the curve indicating the temperatures below which an alloy is wholly solid, just as the "liquidus" indicates the temperatures above which it is wholly liquid.[1]

It is therefore apparent that so long as cooling is slow enough for the comparatively nickel-rich solid deposited in the early stages to absorb additional copper from the liquid as the temperature falls, the final result of the cooling will be a single homogeneous solid solution of the same composition as the liquid mixture employed. The structure of the uniform material thus obtained when viewed in section under the microscope will resemble that of a pure metal, the same polygonal grains being observed. But it should be understood that the absorption of copper by the already solidified portions involves diffusion in the solid state, and—even at such high temperatures—diffusion in the solid state is a very slow process. Consequently, unless the nickel-copper alloy is allowed to cool at a very slow rate, the first solidified portions are likely to remain richer in nickel than the last solidified portions, and the sections will therefore not appear uniform when viewed under the microscope. Thus a quickly cooled nickel-copper alloy, etched with ferric chloride, or chromic acid, appears white at the points where solidification commences, but dark in the parts which solidified last. The light portions are those most rich in nickel, and usually possess a dendritic structure, the dark copper-rich portion filling in the spaces between the fronds (see Fig. E of frontispiece). The contrast is so sharp that it is scarcely surprising that one of the earlier investigators at first thought that the alloy was made up of two essentially distinct parts. However, other etching agents, for instance nitric acid, produce results which show a gradual passage from the nickel-rich centres into the copper-rich fringes.

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[1] The two alternative methods of defining the solidus and liquidus curves are pointed out by C. T. Heycock and F. H. Neville, *Phil. Trans.* **202** [A] (1904), 5–8.

Any nickel-copper alloy, however quickly it may have been cooled, becomes homogeneous and uniform if annealed for some time at 800–1,000° C.; whatever etching agent is employed after such treatment, the metal appears uniform and shows the ordinary granular structure similar to that of a pure metal. This shows that nickel and copper are mutually soluble in the solid state in all proportions. The remarkable contrast between the cored dendritic structure of the copper-nickel alloy "as cast," and the granular structure obtained upon annealing is well shown by Figs. E and F of the frontispiece.[1] But even a very long annealing may not entirely remove all vestiges of dendritic structure; it is probable that the black dots, seen in Fig. F, which are almost invariably met with in annealed specimens of this alloy, represent fragments of the copper-rich zone, which have escaped assimilation.[2]

Since an annealed nickel-copper alloy consists of a single solid solution, it is impossible, on *a priori* grounds, to advance any views as to the probable colour of the various alloys. Actually it is found that a small quantity of nickel notably weakens the red colour of copper, and that alloys containing more than 25 per cent. of nickel are practically white.

Before we leave the subject of nickel-copper alloys, it should be stated that the solid solutions rich in nickel, undergo a further modification, marked by the appearance of magnetic properties, when cooled to comparatively low temperatures (e.g. 20° C. for alloys with 60 per cent. nickel; about 200° C. for alloys with 80 per cent. nickel, and about 350° C. for pure nickel). For the sake of simplicity, no account of this change has been taken in the equilibrium diagram.[3]

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[1] See also F. Adcock, *J. Inst. Met.* **26** (1921), 361, Figs. 1 and 2.

[2] This is the view of Mr. Maurice Cook, who has studied the change from dendritic to granular structure in several alloys. He believes also that the alloys undergo complete recrystallization during the annealing, so that "one dendrite can give rise to more than one polygonal grain." See M. Cook. *Trans. Faraday Soc.* **17** (1922), 524.

[3] For recent work on the magnetic changes in nickel-copper alloys, see R. Gans and A. Fonseca, *Ann. Phys.* **61** (1920), 742.

The **silver-gold** alloys[1] present an equilibrium diagram (Fig. 53) very similar to that of the copper-nickel alloys. A rather different form of equilibrium diagram is obtained, however, in the case of the alloys of **copper** and **gold**[2] (Fig. 54); here again mixed crystals are possible in all proportions, but the liquidus and solidus curves dip down below the melting-points of both metals and actually touch each other at the lowest point P. A liquid alloy having a composition corresponding to P should, on solidification, produce a homogeneous mass without annealing, differing in this respect from any alloy of nickel and copper, and also from the eutectic alloys of Class 1.

If the gold-copper alloys are cooled moderately quickly from below their solidifying point, they consist entirely of ordinary mixed crystals; if, however, they are cooled very slowly—or if the quenched alloys are annealed—certain compounds, Cu_3Au and CuAu, which are only stable below 400°, are produced, and the character of the alloy changes. The upper limits of the stability of the two compounds is shown by curves ABC and DEF respectively (Fig. 54). Consequently, gold-copper alloys do not, strictly speaking, belong to Class 2, although, until 1916, when the

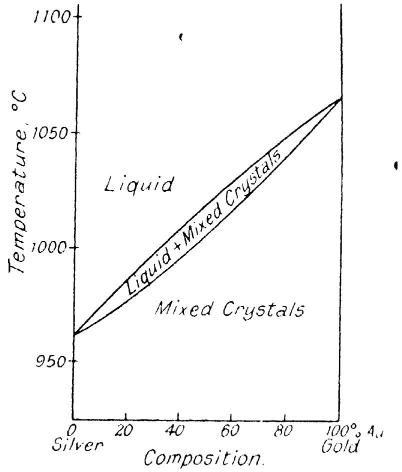

FIG. 53.—The System Silver-gold.

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[1] U. Raydt, *Zeitsch. Anorg. Chem.* **75** (1912), 58.

[2] N. Kurnakow, S. Żemczużny, and M. Zasedatelev, *J. Inst. Met.* **15** (1916), 305.

compounds were discovered, they were believed to do so. They should properly be assigned to Class 5.

The preparation of the equilibrium diagram in alloys of Class 2, as in those of Class 1, can be carried out purely from the examination of cooling-curves. Whilst solidification is taking place the temperature sinks much more slowly than either before or afterwards. The point of inflection of the cooling-curve where solidification commences gives a point on the "liquidus" corresponding to the composition of the alloy under examination; the less well-marked point at the temperature where solidification ceases gives the point on the "solidus." For simple alloys such as those of copper and nickel, the solidus can be plotted by this method with moderate accuracy; but, in many cases, the temperature at which solidification ends is not shown at all definitely on the cooling-curve, and the method can only be regarded as a rough one.

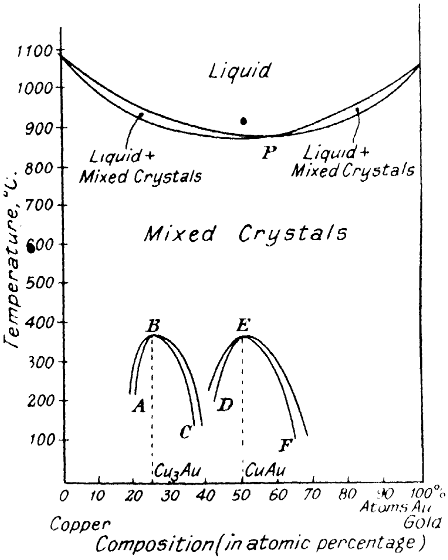

FIG. 54.—The System Copper-gold.

For this reason, a second and far more reliable method of obtaining the solidus curve has been worked out by Heycock and Neville.[1]

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[1] C. T. Heycock and F. H. Neville, *Phil. Trans.* **202** [A] (1904), 6; **214** [A] (1914), 267. The discoverers of the method employed it principally in the study of complicated systems of alloys belonging to Class 5, for instance the bronzes.

A small portion of the liquid mixture is allowed to cool until partl or wholly solid, and is then suddenly cooled ("chilled") to roon temperature; the temperature from which chilling takes place i carefully observed. The micro-structure of the chilled specimer is then studied. If the specimen at the moment of chilling stil contains any liquid, this liquid will solidify very quickly and wil produce a solid of far finer structure than the portion which wa solid before the time of chilling. Consequently the micro-section will show this quickly solidified portion as a fine ground-mass i which the large "primary" crystal skeletons are embedded. If on the other hand, the ingot is entirely solid at the temperature o chilling, the fine ground-mass will not be observed. Therefore

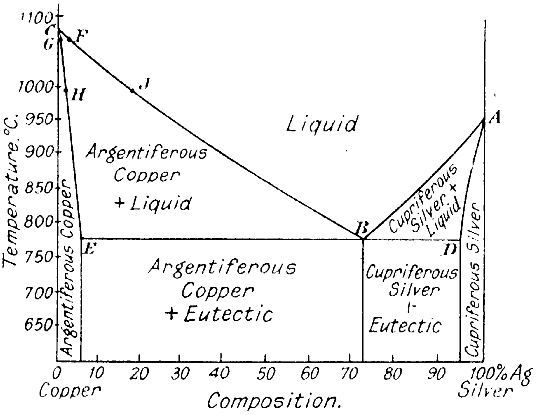

FIG. 55.—The System Copper-silver.

by chilling several samples having the same composition fron different temperatures, the temperature below which the alloy i wholly solid can be determined within narrow limits; in othe words, the point on the solidus corresponding to that compositio can be found.

Class 3. The metals are partially miscible in the solic state. Mixed crystals are possible within certain limits

An example is afforded by alloys of copper and silver[1] (Fig 55).

Pure silver solidifies from the fused state at 962° C. (point A) The solidifying point is lowered by the presence of copper in th fused metal, as is shown by the liquidus curve AB. When silver containing a little copper solidifies, the solid first formed is not pure silver but contains a small amount of copper in solid solution, the composition of the solid in equilibrium with a liquid of any composition being shown by the solidus curve AD. Similarly in the case of molten mixtures rich in copper, solidification starts at temperatures shown by the liquidus curve CB, the composition of the solid produced being indicated by the solidus CE.

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[1] K. Friedrich and A. Leroux, *Metallurgie*, **4** (1907), 293; W. von Lepkowski *Zeitsch. Anorg. Chem.* **59** (1908), 289; compare C. T. Heycock and F. H Neville, *Phil. Trans.* **189** [A] (1897), 57.

Now it follows from the curves that mixtures containing less than 6 per cent. of silver can solidify to a single homogeneous alloy. For consider an alloy containing 3 per cent. silver. This will commence to solidify at the temperature represented by F, depositing crystals of composition represented by the point G. As the temperature falls, the liquid becomes richer in silver, as shown by the curve FJ, whilst the solid, if cooling is sufficiently slow, gradually absorbs silver, as shown by GH. At the temperature represented by the point H, the solid has the composition of the original liquid; in other words the whole has become solid. If cooling is too quick to allow the maintenance of equilibrium (as is usually the case), the alloy produced may not be homogeneous, but it will become homogeneous when annealed.

On the other hand, supposing the original liquid contains 18 per cent. of silver, a homogeneous alloy can in no way be produced. Such a solution will commence to solidify at the temperature represented by the point J, the solid produced having the composition represented by the point H. If the alloy is slowly cooled further, the composition of the liquid changes in the manner shown by the curve JB, and that of the solid as shown by HE. When the temperature 778° C. is reached, the metal is still partly liquid, and at the point B the curve AB is intersected. Consequently, at this point, the remaining metal solidifies as a eutectic of the two solid solutions of composition corresponding to the points D and E; that is, as a eutectic mixture of silver containing 5 per cent. of copper, and of copper containing 6 per cent. of silver.

The structure of the alloys is therefore easily understood. Copper containing less than 6 per cent. of silver becomes homogeneous if annealed sufficiently long; often 40 hours are needed. After annealing the alloy has the polygonal structure and the colour of pure copper. Similarly silver containing less than 5 per cent. of copper differs little in colour and structure from pure silver. But all alloys between these limits remain heterogeneous, however long they are annealed. Those containing 6 per cent. to 73 per cent. of silver consist of primary grains of argentiferous[1] copper separated by, or embedded in, a eutectic. The alloy with 73 per cent. consists of the eutectic alone, whilst alloys with more silver contain—besides the eutectic—grains of cupriferous[1] silver. Fig. D of the frontispiece shows a section of a copper-silver alloy containing 60 per cent. of silver; it consists of dark primary crystals of argentiferous copper embedded in the eutectic.

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[1] Argentiferous = silver-bearing.

The determination of the equilibrium diagram of this class of alloys is carried out in the same manner as those of Class 2. The exact composition corresponding to the eutectic point can be verified by Tammann's method of eutectic times. The positions of the points E and D are often a matter of uncertainty. They are best determined by annealing alloys of different compositions and examining the results microscopically to ascertain whether the alloy has become homogeneous, or whether it contains traces of eutectic between the grains. For instance, an alloy containing 7 per cent. silver, 93 per cent. copper annealed for 40 hours, still shows eutectic between the grains, whilst an alloy containing only 5·75 per cent. of silver becomes homogeneous in that time. Therefore the true position of the point E must fall between 5·75 per cent. and 7 per cent. of silver.

It may appear that alloys of this class differ but little from those of Class 1. As regards mixtures in which the two constituents are present in anything approaching equal amounts, this is true. But where one constituent is present in only a very small quantity, there is a most important distinction. Consider, for instance, a commercial metal containing, as an impurity, 0·5 per cent. of some other metal. The material is really an alloy—although the name may not in practice be applied to it. If the two constituents form an alloy of Class 1, the impurity will be concentrated between the grains as a eutectic, whilst, if the alloy belongs to Class 2 or Class 3, it will be found, in solid solution, uniformly distributed through the grains. The difference between the two cases is of immense importance, as will be seen later, in determining the mechanical and electrical properties of the material; the presence of the impurity between the grains is very liable to cause inter-granular fragility, whilst an impurity in solid solution is generally rather beneficial to the mechanical properties, although detrimental to the electrical properties.

Class 4. Cases in which an intermetallic compound of definite composition is formed.

An example is provided by the alloys of **magnesium and lead**[2] (Fig. 56).

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[1] Cupriferous = copper-bearing.

[2] G. Grube, *Zeitsch. Anorg. Chem.* **44** (1905), 117.

No new principle is introduced in cases in which an intermetallic compound is formed. Lead and magnesium unite to form a definite compound Mg_2Pb. This compound has a melting-point of 550° ; that is to say, the solid compound is in equilibrium with a liquid

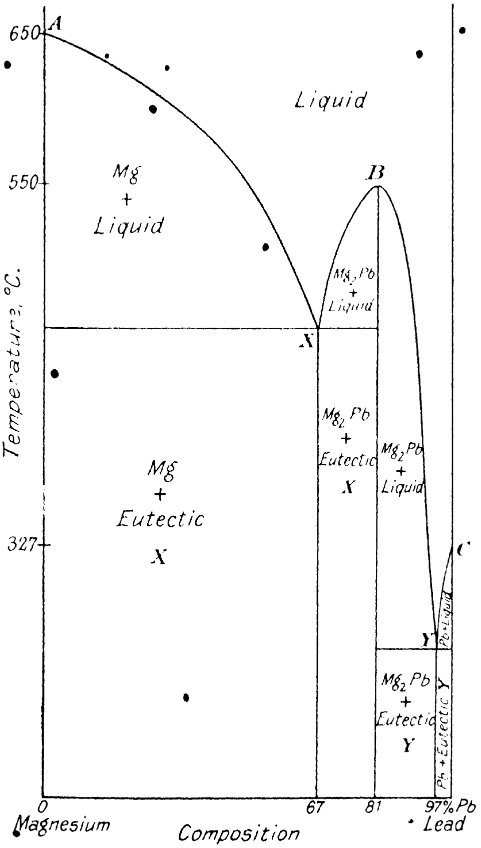

FIG. 56.—The System Lead-magnesium.

of the same composition at that temperature. It may, however, exist in equilibrium with fused metal containing more lead or more magnesium than this amount at lower temperatures, as is shown by the curve XBY. The solid does not retain lead or magnesium in solid solution.

Similarly, pure molten lead solidifies at 327°, but the freezing-point is lowered by the presence of magnesium in the melt, as may be seen from the curve CY; molten magnesium solidifies at 650° C., and the curve AX shows how the solidifying point is lowered by the presence of lead.

It will be obvious from the diagram that a liquid containing less than 67 per cent. of lead will first deposit crystals of magnesium until the residual liquid is of the eutectic composition (67 per cent.) indicated by the point X; the structure of the resultant solid alloy will show large white crystals of magnesium embedded in a dark eutectic of magnesium and the compound Mg_2PG. Freshly prepared alloys with 67 to 81 per cent. of lead, will consist of steel-grey crystals of the compound embedded in the same eutectic; but the compound becomes rapidly oxidized in damp air, darkening considerably. Alloys with 81 to 97 per cent. of lead contain crystals of the compound Mg_2Pb in a lead—Mg_2Pb eutectic ("eutectic Y"), whilst those with 97 to 100 per cent. lead will contain lead crystals together with the same eutectic.

The compound Mg_2Pb has properties quite distinct from those of either metal. It is a brittle mass of metallic appearance, steel-grey in colour and becoming very bright when polished. It is, however, very easily oxidized in damp air; the large crystals soon fall to pieces, yielding a black powder, whilst eutectics containing the compound darken almost instantaneously. The compound decomposes water.

One characteristic of intermetallic compounds is that they frequently solidify—not in dendritic or skeleton growths—but in well developed geometrical forms. In this respect they differ from most of the pure metals. Certain alloys of tin and antimony contain wonderfully perfect cubes of the compound SbSn.

In some alloy-systems more than one intermetallic compound is formed, but this in itself introduces no fresh difficulty. The melting-point curve of the alloys of **copper and magnesium**,[1] which form two compounds Mg_2Cu and $MgCu_2$, has two maxima and three eutectic minima (Fig. 57).

In many metallic substances, compounds between metals and non-metals, such as carbides, phosphides, oxides and sulphides occur; many of these have quite definite compositions, and, in such cases, the alloys may usually be referred to Class 4.

The determination of the equilibrium diagram of Class 4 of alloys presents no special difficulty, being founded upon the study of cooling-curves in the manner described in connection with Class 1.

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[1] R. Sahmen, *Zeitsch. Anorg. Chem.* **57** (1908), 26.

Class 5. The intermetallic compounds have not a constant composition, being capable of including in their crystal-structure excess of one or both components and thus constituting a range of solid solutions.

Fig. 58 shows the equilibrium diagram for the alloys of **gold and magnesium.**[1] There are three well-marked maxima (B, C and D) corresponding to the compositions of the three compounds AuMg, $AuMg_2$, and $AuMg_3$. Of these compounds, the first-named has the highest melting-point, being in equilibrium with a liquid of the same composition as itself at 1,160°. If, however, the liquid

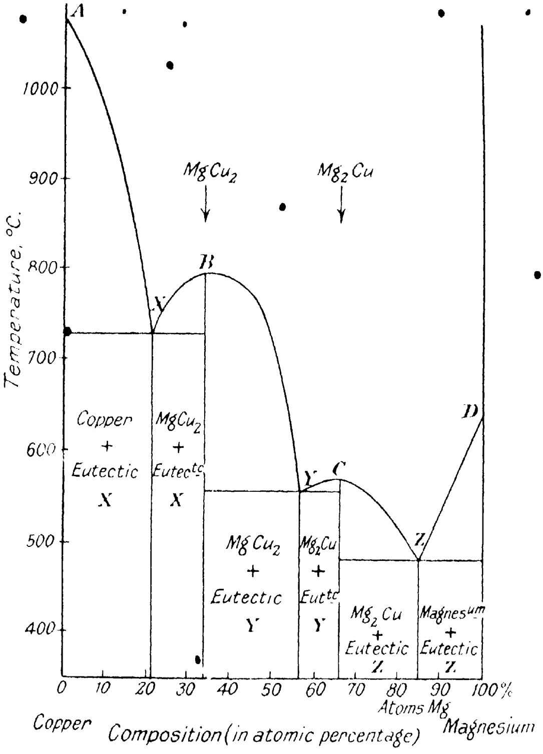

FIG. 57.—The System Copper-magnesium.

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[1] R. Vogel, *Zeitsch. Anorg. Chem.* **63** (1909), 169; G. G. Urasow, *Zeitsch. Anorg. Chem.* **64** (1909), 375; G. G. Urasow and R. Vogel, *Zeitsch. Anorg. Chem.* **67** (1910), 442.

contains either more gold, or more magnesium, than corresponds to the formula AuMg, the melting-point is lowered, as is shown by the liquidus curve XBY; moreover, under these circumstances the solid in equilibrium with the liquid, no longer possesses the composition AuMg, but contains the elements in the proportions shown by the solidus curve PBQ. The mixed crystals formed along this solidus may contain anything between 36 and 60 *Atoms Per Cent.* of magnesium; but, since they have a maximum stability at the exact composition AuMg—that is to say, they have a maximum melting-point corresponding to that composition—it is fair to regard all the crystals of the series as varieties of the com-

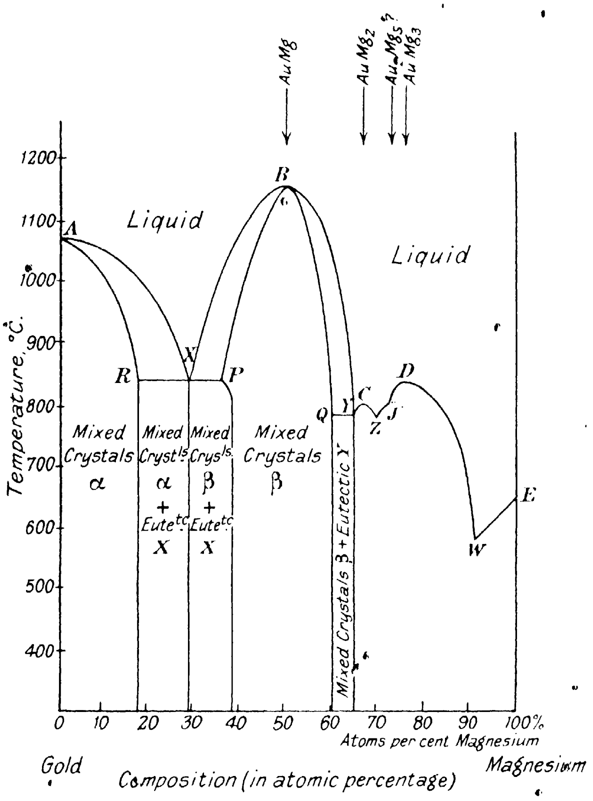

FIG. 58.—The System Gold-magnesium.

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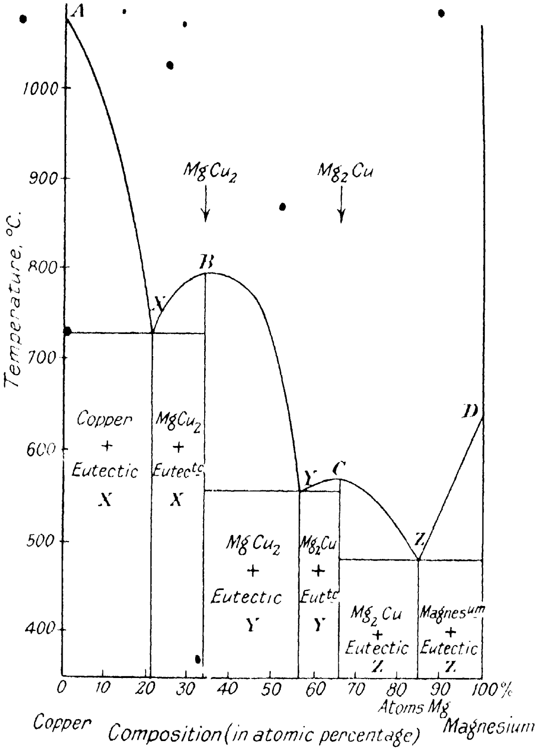

FIG. 57.—The System Copper-magnesium.

D) corresponding to the compositions of the three compounds AuMg, AuMg$_2$, and AuMg$_3$. Of these compounds, the first-named has the highest melting-point, being in equilibrium with a liquid of the same composition as itself at 1,160°. If, however, the liquid absence of any simple formula which can be assigned to the other two maxima leads to the belief that not all solid solutions can be regarded as derived from compounds of simple atomic formula.

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[1] R. Vogel, *Zeitsch. Anorg. Chem.* **63** (1909), 169; G. G. Urasow, *Zeitsch. Anorg. Chem.* **64** (1909), 375; G. G. Urasow and R. Vogel, *Zeitsch. Anorg. Chem.* **67** (1910), 442.

The example just given should be borne in mind, when we pass on to consider the **zinc-copper** alloys, the **brasses** as they are called.[1] The diagram (Fig. 60) is rather complicated, and uncertainty still exists regarding one or two parts of it. The liquidus curve consists of six portions (AB, BC, CD, DE, EF and FG) discontinuous with one another; the corresponding portions of the solidus (AH, BJ, CK, KL, and LM), which are all far from vertical, show how much the composition of the solid solutions varies with the composition of the liquid from which they are deposited.

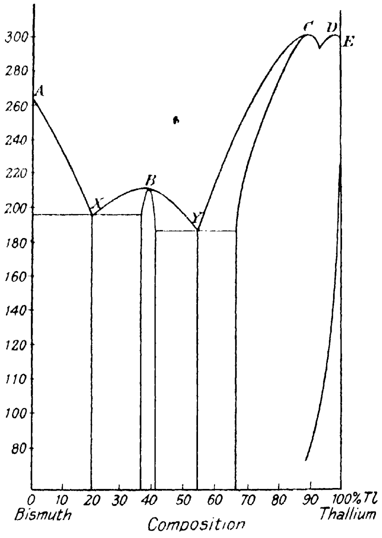

FIG. 59.—The System Bismuth Thallium.

Below the solidus, the alloy is, of course, wholly solid; the necessary information regarding the character of an annealed brass of any known composition at any particular temperature is conveyed by the Greek letters assigned to the different areas of the diagram. Under certain conditions of composition and temperature, a brass may consist of a single homogeneous solid solution; under other conditions, it may consist of a complex of two immiscible solid solutions. For instance, the diagram shows that, at 400° C., alloys containing anything between 0 and 36 per cent. of zinc may consist of a single homogeneous solid solution commonly known as the α-solution, whilst those between 36 per cent. and 47 per cent. of zinc contain two solid solutions, and are not homogeneous. There are at least six types of solid solutions which occur in zinc-copper alloys. They are known as α, β, γ, δ, ε and η. In addition there is another component, β_1, which is thought by Carpenter and Edwards [1] to be a fine eutectoid mixture of α and γ, whilst Hudson [2] and others prefer to regard it as a distinct solid solution. It certainly appears to possess properties of its own,[3] and it is convenient to treat it provisionally as a homogeneous substance, although it is quite likely that the views of Carpenter and Edwards, who regard it as a complex, may ultimately prove to be correct.

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[1] W. C. Roberts-Austen, *Proc. Inst. Mech. Eng.* (1897), 31; E. S. Shepherd, *J. Phys. Chem.* 8 (1904), 421; V. E. Tafel, *Metallurgie*, 5 (1908), 349, 375; H. C. H. Carpenter and C. A. Edwards, *J. Inst. Met.* 5 (1911), 127; O. F. Hudson, *J. Inst. Met.* 12 (1914), 89.

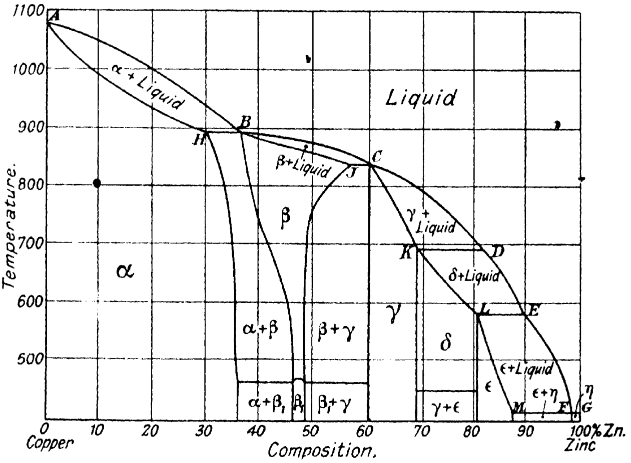

FIG. 60.—The System Copper-zinc (Shepherd's Diagram with Modification suggested by Desch).

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[1] H. C. H. Carpenter and C. A. Edwards, *J. Inst. Met.* **5** (1911), 127; H. C. H. Carpenter, *J. Inst. Met.* **7** (1912), 70; **8** (1912), 51; **12** (1914), 101.

[2] O. F. Hudson, *J. Inst. Met.* **12** (1914), 89. See also C. H. Desch, *J. Inst. Met.* **5** (1911), 171; **12** (1914), 104.

[3] L. Guillet, *Rev. Met.* **11** (1914), 1103. Sir G. Muntz, *J. Inst. Met.* **5** (1911), 182.

Each of these solid solutions has a composition varying between wide limits, as is shown by the diagram; nevertheless, there are certain properties possessed by each of the six solid solutions almost independently of the composition.[1] The α-solution is soft, ductile and malleable; α-brass (i.e. brass containing less than 36 per cent. of zinc) can readily be rolled cold. The β-solution is somewhat harder, stronger, but less ductile, whilst the γ-solution is very hard and very brittle. The so-called "β_1-solution," which may really be a fine mixture of α and γ, is also inclined towards brittleness. Brasses containing 36 per cent. to 47 per cent. of zinc contain β_1 in addition to α, and such brasses are commonly rolled hot. Above 470°, the β_1 changes to β, and rolling can be conducted with impunity. If rolled at too low a temperature, the same brasses are liable to break; the transformation from β to β_1, which occurs below 470°, is sometimes called the "black-hot breaking-point" of brass.

Alloys containing the γ-solution as independent crystals are extremely brittle, and consequently brasses with more than about 50 per cent. of zinc are of no practical use, except, perhaps, for ornamental castings. The δ-solution is also hard and brittle, whilst the ε and η-solutions are somewhat softer, and are said to resemble zinc in their general properties.

The colours of the different solutions are also characteristic; the α-solution is yellow, the β_1-solution is reddish, the γ-solution is white, whilst the ε- and η-solutions are greyish-white or bluish-white, recalling the colour of zinc. In the light of these facts, it is easy to understand the following table, which gives the colours of the alloys of different composition. It will be noticed that the brasses of the β_1 range are more reddish than those which contain more copper:—

100	per cent.	Copper	Red
98-90	,,	,,	Yellow-red
73-63	,,	,,	Yellow
63-50	,,	,,	Red-yellow
49-43	,,	,,	Pinkish-grey
43-41	,,	,,	Silver-white
29	,,	,,	Light grey
22-0	,,	,,	Bluish-white

The use of the Greek letters to represent the different solid solutions has one considerable advantage in that it involves no expresture, a brass may consist of a single homogeneous solid solution; under other conditions, it may consist of a complex of two immiscible solid solutions. For instance, the diagram shows that, at 400° C., alloys containing anything between 0 and 36 per cent. of zinc may consist of a single homogeneous solid solution commonly known as the *α*-solution, whilst those between 36 per cent. and 47 per cent. of zinc contain two solid solutions, and are not homogeneous. There are at least six types of solid solutions which occur in zinc-copper alloys. They are known as *α*, *β*, *γ*, *δ*, *ε* and *η*. In addition there is another component, β_1, which is thought by Carpenter and Edwards [1] to be a fine eutectoid mixture of *α* and *γ*, whilst Hudson [2] and others prefer to regard it as a distinct solid solution. It certainly appears to possess properties of its own,[3] and it is convenient to treat it provisionally as a homogeneous substance, although it is quite likely that the views of Carpenter and Edwards, who regard it as a complex, may ultimately prove to be correct.

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[1] G. H. Gulliver, "Metallic Alloys" (Griffin), p. 275; P. Reinglas, "Chemische Technologie der Legierungen" (Spamer, 1919), pp. 286-296; E. S. Shepherd, *J. Phys. Chem.* 8 (1904), 424.

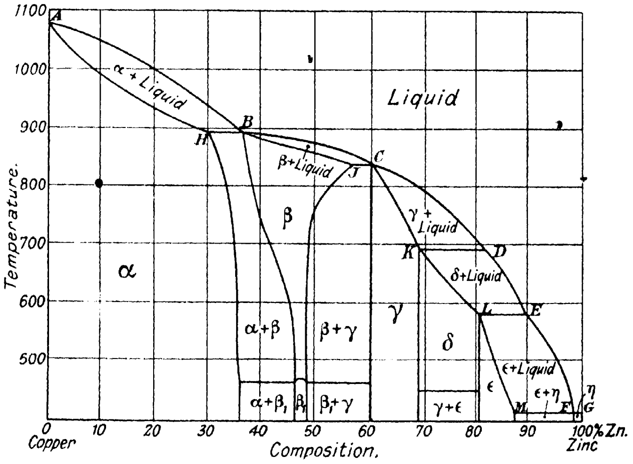

FIG. 60.—The System Copper-zinc (Shepherd's Diagram with Modification suggested by Desch).

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[1] H. C. H. Carpenter and C. A. Edwards, *J. Inst. Met.* **5** (1911), 127; H. C. H. Carpenter, *J. Inst. Met.* **7** (1912), 70; **8** (1912), 51; **12** (1914), 101.

[2] O. F. Hudson, *J. Inst. Met.* **12** (1914), 89. See also C. H. Desch, *J. Inst. Met.* **5** (1911), 171; **12** (1914), 104.

[3] L. Guillet, *Rev. Mét.* **11** (1914), 1103. Sir G. Muntz, *J. Inst. Met.* **5** (1911), 182.

which wrong, and which merely meaningless. Already a comparison of the X-ray patterns obtained with different brasses has shown that α-brasses containing 10 per cent., 30 per cent. and 35 per cent. of zinc give essentially the same pattern, indicating that they are built upon the same system of crystal-architecture, whilst a brass with 40 per cent. of zinc, which contains the β-constituent, gives quite a different pattern.[1]

The equilibrium diagram of the brasses is by no means the most complicated among the diagrams of different systems of alloys. But even diagrams which appear at first sight most formidable, are easily understood after a little study. The reader will, however, appreciate the amount of patience which it must have required to work out some of these systems, and he will not be surprised to note that disagreement—similar to that prevailing over the question of the nature of β_1-brass—exists in many other cases. It is impossible to give any detailed description of the processes employed to obtain a diagram of a complex system, but it is worth while to recall three valuable methods which have already been mentioned.

(1) The first "kink" upon a cooling curve gives a point on the "liquidus," and subsequent kinks indicate other transformations occurring at lower temperatures.

(2) Where a eutectic occurs, the comparison of the eutectic times of alloys having different compositions, allows the exact composition of the eutectic to be calculated (Tammann's method).

(3) By chilling alloys from different temperatures, information regarding the structure at the temperature of chilling is obtained (Heycock and Neville's method); this is especially useful in determining the position of a "solidus" curve.

Mechanical and Electrical Properties of Alloys. In the examples of alloys discussed above, two of the properties, the melting-point and the colour, have been kept especially in view. In considering the brasses, it has been convenient also to refer to the mechanical properties. It is necessary now to discuss the variation of mechanical properties with the composition of alloys in general.

The mechanical properties of the alloys of Class 1 do not differ very strikingly from those of the pure components.[2] This is quite to be expected, for the alloys are really merely conglomerates of the two metals. If both the components are malleable, the alloy will be malleable; if both the components are brittle, the alloy will be brittle. If one component is malleable and the other is brittle, the properties will depend upon the character of the eutectic; the eutectic of lead and bismuth, for instance, is scarcely malleable, and the presence of bismuth in lead greatly reduces the malleability of that metal. Other properties of the alloys of this class—such as electrical conductivity—usually fall between the values of the two components, as would be expected.

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[1] S. Nishikawa and G. Asahara, *Phys. Rev.* **15** (1920), 40.

[2] L. Guillet, *Comptes Rend.* **144** (1907), 1273.

In several metals, which are serviceable when pure, the presence of small amounts of certain impurities between the grains has a most disastrous effect in causing inter-granular weakness. Copper containing a trace of oxygen, which exists as a eutectic of copper and cuprous oxide at the boundaries of the grains, is quite brittle. Likewise copper containing a small amount of bismuth, which collects at the grain boundaries, is very fragile; here the "eutectic" consists of practically pure bismuth.[1]

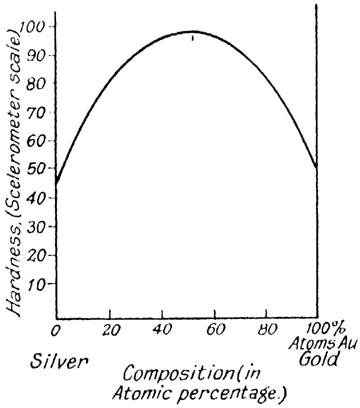

FIG. 61.—Hardness of Gold-Silver Alloys.

When, as in alloys of Classes 2, 3, or 5, mixed crystals containing both metals occur, the alloys are usually harder and more unyielding than either component. A very small quantity of a second element in a metallic crystal raises the hardness in a most marked degree.[2] Fig. 61 shows the hardness curve of the alloys of silver and gold, metals which can form solid solutions in all proportions. It will be seen that the hardness of the alloys is for the most part far greater than that of either component; a maximum hardness is reached in this case—and indeed in many others—when the alloy contains atoms of both metals in nearly equal numbers.

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[1] K. Jeriomin, *Zeitsch. Anorg. Chem.* **55** (1907), 412.

[2] N. S. Kurnakow and S. F. Žemčužny, *Zeitsch. Anorg. Chem.* **60** (1908), 1.

The hardness of a material gives a rough idea of the tensile strength, which is clearly greater for alloys of this class than for the pure component metals. On the other hand, the ductility of the alloys is generally less than that of the components. As to whether an alloy will be more serviceable than the pure metals will vary in different cases, and will, of course, also depend on the use to which the material is to be put. If—in our natural desire to increase the tensile strength—we allow the ductility and malleability to be reduced too far, the alloy will be liable to break if subjected to momentary shocks of exceptional character, instead of yielding to them. What is generally required of a material is "toughness," a combination of strength and ductility. The useful alloys are mostly those which possess this qualification.[1] Most of the important industrial alloys—Brass, Bronze, Monel Metal, Nickel Silver, and many of the new light aluminium alloys—consist mainly of solid solutions. The commonly practised addition of copper to gold serves to make the metal harder and more resistant to wear, mixed crystals of gold and copper being produced.

On the other hand, where a soft, ductile and malleable material is required, a specially pure form of metal is usually sought. The small amount of impurity usually found in commercial metals—whether present in solid solution or as a eutectic between the grains—generally interferes with these qualities.

The cause of the unyielding character of mixed crystals—as compared with the crystals of a single metal—has been the subject of much discussion.[2] The fact that the alloys have a lower ductility and greater strength than their components is a sign that—for some reason—gliding does not occur readily in the mixed crystal. In the crystal in which all the atoms consist of silver, one layer can slide readily over another; the same is true if all the atoms are gold. But if some of the atoms are gold and others silver, the sliding seems to become less easy. If the atoms of gold were different in size from those of silver this would not be difficult to understand; but, as a matter of fact, the atomic volume of silver is almost exactly equal to that of gold.

A satisfactory explanation is provided if the assumption is made that the force existing between unlike atoms is always greater than that holding together two atoms of the same kind[3]; it would follow from this assumption that the force needed to divide a mixed crystal containing both silver and gold atoms into two halves along a cleavage plane—or even to make one half glide upon the other—will be greater than the corresponding forces required to cause cleavage or gliding in a pure metal. The assumption required appears to be entirely in accordance with the view of inter-atomic force which has already been sketched in the Introduction. Moreover the theory explains adequately why the greatest hardness is generally met with when the mixed crystal contains an equal number of atoms of each component.

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[1] See F. C. Thompson, *Trans. Faraday Soc.* **12** (1917), 23; T. Turner, *J. Inst. Met.* **18** (1917), 92, 93.

[2] See especially C. H. Desch, *Trans. Faraday Soc.* **10** (1915), 251.

[3] G. Tammann, "Lehrbuch der Metallographie" (Voss) (1914 edition), pages 331 and 332. A rather similar view is clearly stated and developed by W. Rosenhain, *Proc. Roy. Soc.* **99** [A] (1921), 196. See also Z. Jeffries and R. S. Archer, *Met. Chem. Eng.* **26** (1922), 249.

Another property in which an alloy of the mixed-crystal type (Classes 2, 3 and 5) always differs from the component metals is the **electrical conductivity.**[1] Pure metals are good conductors of electricity; mixed crystals conduct far less well. The curve indicating the electrical resistance of alloys of two metals which form a complete series of mixed crystals resembles closely the curve of hardness. The curve showing the conductivity is naturally like the hardness curve inverted, and has normally the form of a broad U. Fig. 62 shows the conductivity curve of the silver-gold series of alloys.[2] The practical effect of impurities upon the conductivity of a metal is important. Copper required for use in electrical work must be of the purest character; as little as 0·35 per cent. of arsenic in solid solution reduces the conductivity by a half.[3] Aluminium, antimony, phosphorus, and silicon, which likewise form

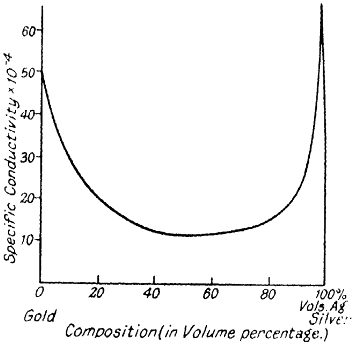

FIG. 62.—The Electrical Conductivity of Gold-Silver Alloys.

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[1] Much useful information on this subject has been collected by A. L. Norbury, *Trans. Faraday Soc.* **16** (1921), 570.

[2] W. Guertler, *Zeitsch. Anorg. Chem.* **51** (1906), 403.

[3] N. Puschin and E. Dischler, *Zeitsch. Anorg. Chem.* **80** (1913), 65.

solid solutions with copper, have also a serious effect on the conductivity. On the other hand, the presence in copper of bismut lead, tellurium, and selenium, impurities which do not enter th copper crystals, but accumulate as a eutectic at the boundarie of the grains, are much less deleterious to the electrical propertie It is interesting to note that it is just these substances, which hav comparatively little effect on the conductivity, that cause mechanical weakness, and a tendency to inter-granular fracture.

Before discussing the cause of the relatively poor conductivit of alloys, it is necessary to adopt some view regarding the mechanis of the passage of electricity through a pure metal. Lindemann' theory appears to be most helpful.[1] According to Lindemann, th loosely bound electrons of the metallic atoms (i.e. the valenc electrons) exist in the crystal structure in the spaces between th atoms, forming a second lattice of electrons "interleaved" wit the lattice of atoms.[2] When an E.M.F. is applied, the electro lattice moves relatively to the atom-lattice, thus causing the conduction of electricity through the metal. Now in a pure meta where all the atoms are alike, the electrons will be equally attracte —or equally repelled—by all the atoms, and will therefore be fre to move easily between the atoms. True, if the atoms are in state of vibration, the passage of the electrons will be hindere somewhat; and accordingly there is, even in pure metals, a considerable electrical resistance at high temperatures, although a very low temperatures (e.g. 3° Absolute) this resistance become almost negligibly small. But if the atoms are of two separat kinds, the regularity of the two inter-penetrating lattices will b disturbed and the free passage of the electrons through the atomi lattice will be obstructed considerably. It follows that mixe crystals will conduct less well than pure crystals at the same temperature.

The physical properties of alloys of Class 4 still remain to b considered; these contain intermetallic compounds of definit composition. Such compounds—like Mg_2Pb—are usually har but are generally extremely brittle. The same statement applies to many of the compounds formed between metals and non-metals, such as iron carbide, which are important components of alloys. Apparently in such compounds the natural planes along which the atoms are arrayed behave rather as planes of cleavage than as planes of gliding. It is of interest to recall the fact that in ordinary compounds such as sodium chloride, where the component elements are essentially dissimilar to one another, the same observation holds good.

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[1] F. A. Lindemann, *Phil. Mag.* **29** (1915), 127. See also W. C. McC. Lewi *Chem. Soc. Ann. Rep.* **17** (1920), 7, 8. The theory of the diminished conductivity of mixed crystals which can be developed from Lindemann's view is closely analogous to the theory of the increased hardness given by W Rosenhain, *Proc. Roy. Soc.* **99** [A] (1921), 196.

[2] According to one view, due to G. Borelius, *Phil. Mag.* **40** (1920), 74 the structure of metallic copper may be compared to that of a salt like sodiu chloride. If we imagine that the places occupied by sodium atoms are fille by copper atoms, and the places occupied by the chlorine atoms are filled b free electrons, we obtain a possible picture of metallic copper; it is cle that not only are the copper atoms placed upon a face-centred cubic lattic but the electrons also form a second face-centred cubic lattice interpenetratin the first.

As a result, alloys in which these intermetallic compounds occur—other than in a eutectic—are brittle and, in most cases, of no commercial importance. White cast iron, which contains a considerable amount of free iron carbide (although of importance as the raw material for making malleable cast iron), is too brittle to be used for most purposes in the unmodified state.

Whilst the intermetallic compounds of constant composition are generally undesirable in commercial materials, the numerous industrial alloys of Class 5 contain solid solutions which (as already explained) may probably be regarded as being intermetallic compounds containing excess of one or other constituents. The properties of alloys of this class resemble those of Classes 2 and 3 rather than those of Class 4. The mechanical properties of the brasses—which belong to Class 5—have already been considered.

Summary. Alloys formed between two metals may be classified according as they form :—

(1) No mixed crystals (gold-thallium alloys).
(2) A complete range of mixed crystals (copper-nickel, silver-gold, copper-gold).
(3) Limited range of mixed crystals (copper-silver).
(4) Intermetallic compounds of fixed atomic composition (magnesium-lead, magnesium-copper).
(5) Intermetallic compounds of variable composition, forming a range of "solid solutions" (magnesium-gold). Controversy prevails as to whether some of the "solid solutions" (e.g. in the brasses) are related to definite compounds or not. Certainly in the case of bismuth-thallium alloys, they do not appear to be so related.

Like metals tend to form *mixed crystals* in which the atoms of both play the same part in the crystal structure; *unlike* metals form *intermetallic compounds* in which the atoms appear to have different rôles. The formulæ of intermetallic compounds are not determined by the ordinary valency of the metal.

The equilibrium diagrams of the various systems are worked out by the study of cooling curves taken on mixtures of known composition, supplemented by Tammann's method of eutectic times and the Heycock-Neville method of quenching from a know temperature.

In general, the structure of alloys of Classes (1) and (4) wi consist of primary crystals embedded in a eutectic ; alloys of Clas (2) will be homogeneous when annealed (showing polygonal structure), but may appear heterogeneous when cooled rapidly, displaying dendritic "coring." Alloys of Classes (3) and (5) will b homogeneous or heterogeneous according to their composition.

The physical properties of alloys of Class (1) are usually intermediate between those of the pure metals, but this is not the cas in the other classes. Solid solutions and mixed crystals are harde stronger and less ductile than the pure components ; this is explained on the assumption that the attractive force between unlik atoms exceeds that between like atoms. In the alloying of metal for technical purposes, "toughness" (a combination of grea strength and moderate ductility) is generally required. Mos technically important alloys belong to Classes (2) and (5).

The electrical conductivity of mixed crystals is less than tha of the component metals. Impurities in copper affect the mechanical and electrical properties in a different way. Those that collec between the grains cause inter-granular weakness, but do no seriously affect the conductivity ; those that pass into solid solutio do not affect adversely the mechanical qualities, but reduce th conductivity to a very marked extent.

Intermetallic compounds of definite composition are generall brittle, and most of the alloys containing them are of little practica importance.

PART II

THE STUDY OF THE IONIC STATE (ELECTRO-CHEMISTRY)

CHAPTER V

THE PASSAGE OF ELECTRICITY THROUGH A SOLUTION

Mechanism of Electrolysis. When a current of electricity passes through a metallic conductor, the metal undergoes no change apart from a slight rise of temperature. But when electricity passes through a solution, it produces two other marked effects; firstly, it causes **motion** within the liquid, and secondly, it causes **decomposition**. There is every reason to think that the two effects are closely connected.

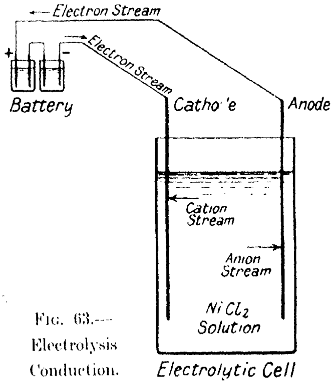

Fig. 63.—Electrolysis Conduction.

The decomposition is easily observed. If two plates, or "electrodes," of platinum are immersed in a green solution of nickel chloride, and are joined by wires to an electric battery (Fig. 63), a deposit of metallic nickel is produced on the negative electrode or cathode, whilst chlorine gas is evolved at the positive electrode or anode. The decomposition can be summarized by the equation,

$$NiCl_2 = Ni + Cl_2$$

But, according to the Ionization Theory, which has been sketched in the introduction, the nickel and chlorine exist in the solution, before ever the current is passed through it, as virtually separate "ions." The nickel ion consists of a nickel atom bereft of two electrons; it possesses, therefore, two positive charges and is written $Ni^{\cdot\cdot}$. The chlorine ion is a chlorine atom with one extra electron; it possesses, therefore, a negative charge, and is written Cl'. The two ions are generally supposed to be in equilibrium with a certain quantity of undissociated nickel chloride molecules, thus

$$NiCl_2 \rightleftharpoons Ni^{\cdot\cdot} + 2Cl'$$

Before the electric current is passed through the solution, the nickel and chlorine ions are moving about separately through the solution—by virtue of the ordinary thermal agitation—just as though they were separate molecules. When the electrodes are immersed in the solution, and an E.M.F. is applied by connection with the electric battery, a "directive influence" is exerted upon this thermal movement, which has hitherto taken place with equal facility in all directions. The positively charged nickel ions commence to move more readily towards the negative pole or cathode than in the opposite direction, and the outcome is that—on the whole—there is movement of nickel ions towards the cathode; similarly, the chlorine atoms commence to move—on the whole—towards the anode. The undissociated nickel chloride molecules, being uncharged, take no direct part in the movements.

The electric battery, when furnishing a current, pushes a steady stream of electrons outwards from the so-called negative terminal, and sucks in a steady stream at the so-called "positive" terminal. Now consider the layer of solution quite close to the cathode of the electrolytic cell. Here the nickel ions will be attracted on to the electrode surface itself. Within the cathode there is a supply of electrons arriving from the negative terminal of the battery, and the nickel ions which are arriving from the solution are each furnished with two electrons, and thus become atoms of metallic nickel, which array themselves after an orderly fashion to form a layer of crystalline nickel. The electrons needed to convert the nickel from the ionic to atomic form continually uses up the supply of electrons on the platinum, and the constant stream of electrons from the battery is simply required to keep it replenished. Using the symbol e to represent an electron, the cathodic reaction can be written:—

$$Ni^{\cdot\cdot} + 2e \rightarrow Ni$$

Meanwhile, at the anode, chlorine ions, bearing their extra electrons, are attracted by electrical forces on to the electrode, where the extra electron is given up and is sucked away into the platinum by the electro-motive force of the battery. The chlorine atoms left uncharged, join in pairs to form molecules, which collect together as bubbles of chlorine gas. The anodic reaction can thus be written in two stages :—

$$\begin{aligned} 2\mathrm{Cl}' &= 2\mathrm{Cl} + 2e \\ 2\mathrm{Cl} &= \mathrm{Cl}_2 \end{aligned}$$

It will be seen, therefore, that the apparent passage of electricity through a solution is not due to the passage of free electrons from cathode to anode, but is dependent upon the movement of two streams of charged ions, one moving to the cathode and one to the anode. The transformation of ions to the atomic state at the cathode results in the absorption of the excess of electrons which is provided by the electric current, whilst, at the anode, the discharge of the negative ions results in the production there of a corresponding excess of electrons. From the electrical—as opposed to the chemical—point of view, the result is exactly the same as though the electricity were passing straight through the solution from cathode to anode, and it is possible, therefore, to assign a definite " electrical conductivity " to the solution.

In the case of nickel chloride, the substances produced by electrolysis have the same composition—apart from the question of excess or defect of electrons—as the ions which are discharged. Often, however, important secondary changes occur at the electrodes. Many metals react with water, as soon as they are produced at the cathode, yielding hydrogen and a hydroxide ; similarly, the anions of the salts containing oxygen often react with water after giving up their electrons, producing oxygen and an acid. Thus sodium sulphate (Na_2SO_4) undergoes the following changes on electrolysis :—

$$\begin{array}{lll} \text{(1) \textit{At the Cathode}} & 2\mathrm{Na}^{\cdot} + 2e & = 2\mathrm{Na} \\ & 2\mathrm{Na} + 2\mathrm{H_2O} & = 2\mathrm{NaOH} + \mathrm{H_2} \\ \text{(2) \textit{At the Anode}} & \mathrm{SO_4}'' & = \mathrm{SO_4} \quad + 2e \\ & \mathrm{SO_4} + \mathrm{H_2O} & = \mathrm{H_2SO_4} \quad + \mathrm{O} \end{array}$$

The final result of the decomposition is that the solution becomes alkaline round the cathode and acid round the anode, whilst hydrogen and oxygen gases are respectively liberated at the two electrodes.

In the cases considered so far, it is assumed that the electrode material takes no part in the change ; where a platinum electrode is concerned, this is—at least to all outward appearance—true. But supposing that in the electrolysis of nickel chloride a nickel anode were used, the chlorine produced would then attack the nickel yielding nickel chloride, which would dissolve in the solution, replenishing the nickel lost by deposition of metal upon the cathode. The nickel chloride, on dissolving, would split up largely into ions.

In such a case, the anodic reaction can thus be expressed in three stages :—

$$2Cl' = 2Cl + 2e$$
$$2Cl + Ni = NiCl_2$$
$$NiCl_2 = Ni^{\cdot\cdot} + 2Cl'$$

Adding these three equations, and eliminating what is common to both sides, we get :—

$$Ni = Ni^{\cdot\cdot} + 2e$$

Thus the final result of the change, where a "soluble anode" is used, is that the atoms of the anode metal pass into the ionic condition, leaving behind their electrons, which are sucked away by the electromotive force of the battery. It is possible that the simple equation

$$Ni = Ni^{\cdot\cdot} + 2e$$

actually represents events occurring at a soluble anode as truly as the three-stage reaction which was first suggested. It may be that the nickel to a large extent enters the solution spontaneously, instead of waiting to be attacked by the discharged chlorine. At present, however, there is little exact knowledge of what occurs at the electrode boundary; it is impossible to say how far the chlorine "crosses the boundary to carry off the nickel," or how far the nickel crosses it spontaneously in the opposite direction; possibly both nickel and chlorine advance half-way across the boundary to meet each other.

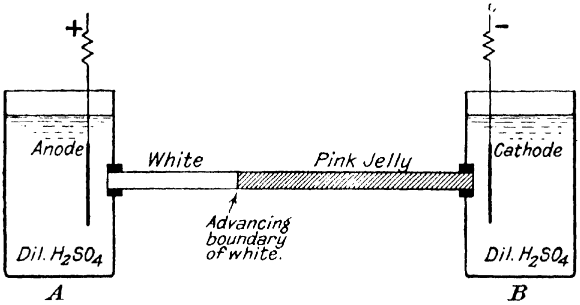

FIG. 64.—Experimental Demonstration of Ionic Movement.

Experimental Demonstration of Ionic Movement. It has been stated that an electric current passing through a solution causes not only decomposition at the electrodes, but also movement of the dissolved materials throughout the body of the solution; the ionic theory attributes the movement and the decomposition to the same cause.

The movement can be experimentally demonstrated in many ways. Two vessels A and B (Fig. 64) containing dilute sulphuric acid may be connected by a tube filled with a jelly made of agar-agar containing sodium chloride and a trace of phenol-phthalein rendered pink with alkali.[1] The vessels contain two platinum electrodes, and when a current is passed between them through the jelly, hydrogen ions from the anodic vessel A commence to move towards the cathode; as they pass through the jelly they neutralize the hydroxyl ions of the alkali and thus destroy the pink colour of the phenol-phthalein. The advance of the white region along the tube gives a method of measuring the velocity of movement of the hydrogen ions.

The movement of the other ions through jelly under the influence of the electric current can be followed if suitable indicators are used.[2] If the vessel A (Fig. 64) contains barium chloride solution, and the jelly contains sodium chloride, together with a trace of sodium sulphate, the advance of the barium ions is recognized by the cloudiness due to the insoluble barium sulphate which is formed as they advance. Conversely, if the vessel B contains sodium sulphate, and the jelly contains sodium chloride and a trace of barium chloride, the velocity of the movement of the $(SO_4)''$ ions can be measured in the same way.

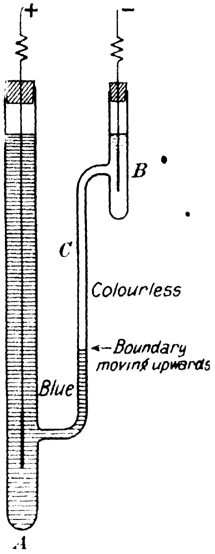

Fig. 65.—The Measurement of the Velocity of a Coloured Ion (Whetham's Method).

If the ion whose movement is being studied is itself coloured, it is possible to dispense with an indicator; furthermore, if the tube connecting the two vessels is vertical, and one of the solutions employed is slightly heavier than the other, the jelly may be dispensed with also. Whetham [1] used the apparatus shown in Fig. 65 to measure the velocity of the copper ion ($Cu^{\cdot\cdot}$); the vessel A is filled with copper chloride solution, whilst the vessel B is filled with ammonium chloride solution; each solution contains a trace of ammonia, which serves to bring out a deep blue colour where copper is present. The boundary between the two solutions in the vertical connecting tube C is marked by the sharp termination of the blue colour. When an E.M.F. is applied between the electrodes in A and B, the blue colour commences to extend upwards along the tube, and the rate at which the boundary travels measures the velocity of the copper ion. In the same way the velocity of the orange anion of potassium dichromate $(Cr_2O_7)''$ has been measured. It is found that the velocities of the $(Cr_2O_7)''$ ions when measured in a jelly and in an ordinary liquid solution, do not seriously differ, and this fact gives support to the numbers obtained for colourless ions, which can only be arrived at by the use of jelly.

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[1] Sir O. Lodge, *Brit. Assoc. Rep.* **56** (1886), 396. The general principles of these methods are well discussed by H. C. H. Whetham, "Theory of Solution" (Cambridge University Press, 1902), pp. 216–226.

[2] W. C. D. Whetham, *Phil. Trans.* **186** [A] (1895), 507.

It is found that the velocity is in all cases proportional to the potential gradient. The velocity under "unit potential gradient" —that is, 1 volt per cm.—is characteristic of the ion, and is called the "**mobility.**" The following table shows some of the numbers obtained for the mobilities of different ions:—

Ion.	Symbol.	**Mobility** (cms. per sec.).
Hydrogen	$H^{\cdot}$	0·0026
Copper	$Cu^{\cdot\cdot}$	0·00031
Barium	$Ba^{\cdot\cdot}$	0·00039
Silver	$Ag^{\cdot}$	0·00049
Sulphate	$(SO_4)''$	0·00045
Bichromate	$(Cr_2O_7)''$	0·00047

It will be observed that the hydrogen ion is much more mobile than any of the others. This is easily understood in view of its extreme lightness.

The mobilities of certain ions, such as those of potassium and chlorine, appear to be fairly independent of the concentration, and of the presence of other ions; often, however, the mobility falls off, as the concentration increases. This may be due in part to the fact that the viscosity of the liquid increases with the concentration, and therefore causes an increased resistance to the motion of the ions. There are, however, two other and more important causes which will be considered more fully at a later stage, but which may be indicated at this point. Firstly, it is thought that in a concentrated solution, only a portion of the molecules are dissociated into independent ions; any given ion will only be in a free state for part of the time, since periodically it will combine with other ions of the opposite kind to form undissociated molecules. Whilst in the combined state, there is no reason why it should move towards one electrode rather than to the other; consequently—owing to these "lapses" into the non-dissociated condition—the progress towards the electrode to which it is moving will be less rapid. Secondly, it is fairly certain that free ions, in a concentrated solution, drag along with them undissociated molecules, and, for this reason, have their mobility reduced. In a concentrated solution of cadmium iodide, it is found that the metal, as a whole, moves, not towards the cathode, but towards the anode; this is commonly explained by the fact that the iodine ions (I') carry with them undissociated molecules of CdI_2, possibly forming definite complex ions $[CdI_3]'$.

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[1] W. C. D. Whetham, *Phil. Trans.* **184** [A] (1893), 337; **186** [A] (1895), 507. A method of determining the velocity of colourless ions without the use of an indicator is given by O. Masson, *Phil. Trans.* **192** [A] (1899), 331.

It is at the same time necessary to point out that, in dilute solutions, the ions may drag along with them molecules of solvent; it is quite certain that a transport of water does occur when the ions move towards the electrodes,[1] and if the two sets of ions drag along different amounts of water, the resulting transport of water towards one electrode can be measured. Many authorities think that the ions are definitely hydrated, i.e. surrounded with an "envelope" of water molecules, which move along as an essential part of the ion. This notion has been adopted in order to explain the fact that the ions of metals possessing the highest atomic volume are not always the least mobile. For instance, the caesium atom is much bigger than the atom of lithium and it might be expected that the frictional resistance opposing the movement towards the electrode would be greatest in the case of the caesium ion; in practice, however, it is found that the caesium ion has a higher mobility than the lithium ion. One possible explanation is that, although the caesium *atom* is undoubtedly bigger than that of the lithium *atom*, it does not necessarily follow that the caesium *ion*—that is, the atom without the valency electron—has a bigger radius than the lithium *ion*.[2] It is more usual to accept the view already suggested, and to assume that the ions are hydrated, the lithium ion having a larger amount of attached water, and being in consequence really bigger than the less hydrated ion of caesium.[1] It is, however, not necessary to assume the existence of a definite number of water molecules permanently attached to the ion; it is more probable that the ions drag a certain amount of water with them when they move towards the electrodes, by virtue of electrical forces, and that the drag is greatest in the case of the lithium ion, which is consequently impeded more in its migration than the heavy caesium ion.[2]

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[1] R. Remy, *Zeitsch. Phys. Chem.* **89** (1914–15), 467, 529. See also H. J. S. Sand, *Trans. Faraday Soc.* **15** (1919), 94.

[2] See F. A. Lindemann, *Trans. Faraday Soc.* **15** (1919), 166.

Faraday's Law. Since every metallic ion carries a charge corresponding to one, two, three, or possibly four electrons, according to the valency of the atom, it is clear that a simple relation must exist between the current which passes (or, at least, appears to pass) through the solution, and the amount of material decomposed.

The atomic weights of any two metals, expressed in grams, must contain equal numbers of atoms; for example, 65·37 grams of zinc contain the same number of atoms as 107·88 grams of silver. But zinc is divalent; the zinc atom has, therefore, two more electrons than the zinc ion ($Zn^{\cdot\cdot}$), whilst, silver being univalent, the silver atom has only one more electron than the silver ion ($Ag^{\cdot}$). If we define the **Gram-Equivalent Weight** as the

$$\frac{\text{Atomic Weight expressed in grams}}{\text{Valency}}$$

a little consideration will show that the conversion of one Gram-Equivalent of any two substances from the ionic to the atomic state will require the same number of electrons. For instance, it will require as great a quantity of electricity to deposit $\frac{65·37}{2}$, i.e. 32·68 grams of zinc on the cathode as to deposit 107·88 grams of silver.

This result can be expressed as a general law, which was first experimentally demonstrated by Faraday. It can conveniently be stated in the following form: "The quantity of electricity required to deposit the gram-equivalent weight of any metal at a cathode is equal to 96,580 coulombs; that is, roughly, to 26·8 ampere-hours." It should be added that the same quantity of electricity is involved when one gram-equivalent of a metal is dissolved at a soluble anode.

The statement of the law just given is subject to one rather important proviso, namely that the whole of the electricity is utilized in the deposition—or the dissolution—of the metal under consideration. If, however, the deposition of zinc is conducted in rather acid solution, and the current causes at the cathode, not only the production of zinc, but also the evolution of hydrogen gas, then the passage of 96,580 coulombs will clearly not lead to the deposition of the full 32·68 grams of zinc. But it is important to note that this is not due to any failure of Faraday's Law; for if the hydrogen evolved is measured and the zinc deposited is weighed, it is found that together they amount to one gram-equivalent for every 96,580 coulombs employed.

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[1] R. Lorenz, *Zeitsch. Phys. Chem.* **73** (1910), 252. Other independent arguments in favour of the hydration of ions are put forward by W. R. Bousfield and T. M. Lowry, *Trans. Faraday Soc.* **3** (1907–8), 123; also by E. Newbery, *Trans. Chem. Soc.* **111** (1917), 470.

[2] The reader should consult the very interesting papers on the subject by M. Born, *Zeitsch. Elektrochem.* **26** (1920), 401; *Zeitsch. Phys.* **1** (1920), 221.

If our desire is to deposit zinc, it is clear that the part of the current expended in the production of hydrogen is current wasted. It is useful to express the amount of metal actually produced as a percentage of that which would be calculated from Faraday's Law on the assumption that no current is wasted on secondary reactions: this percentage is known as the **current efficiency.** If, for instance, after passing a current of one ampere for 26·8 hours, we have obtained only 30 grams of zinc, instead of the theoretical 32·68 grams, the current efficiency is

$$\frac{30}{32{\cdot}68} \times 100 = 91{\cdot}8 \text{ per cent.}$$

Silver Coulombmeter. If it is possible to find a case in which the whole of the electricity is employed in depositing a single metal—in other words, if a deposition-cell can be designed having a current efficiency of 100 per cent.—then the amount of metal deposited upon the cathode can be used to measure the total quantity of electricity which has passed through the cell. Under suitable conditions,[1] the deposition of silver from a solution of silver nitrate is absolutely quantitative, no electricity being used up in subsidiary reactions. A silver nitrate cell can therefore be used as a "**coulombmeter**"; the increase in the weight of the cathode upon which silver has been deposited can be used to indicate the number of coulombs which have passed through the cell during the deposition.

The deposition of mercury has also been used for the measurement of the quantity of electricity; it has the advantage that the mercury can be measured by volume instead of by weight. For rough purposes, coulombmeters in which copper is the metal deposited have also been used.

Conductivity of Solutions. The measurement of the conductivity of a solution is a matter of some little importance.

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[1] Described by T. W. Richards and G. W. Heimrod, *Zeitsch. Phys. Chem.* **41** (1902), 302. See also T. W. Richards and F. O. Anderegg, *J. Amer. Chem. Soc.* **37** (1915), 7.

Difficulties arise when attempts are made to use continuous current—such as is obtained from an ordinary electric battery—for measuring the conductivity of an electrolyte, because when such a current has passed for a very short time through a liquid, a "back E.M.F." due to polarization is set up, which tends to diminish the current passing through the cell. This phenomenon, which will be explained more fully in subsequent chapters, led early experimenters to doubt whether electrolytes really obeyed Ohm's Law. It is now known that, if "polarization" can be avoided, Ohm's Law is obeyed, and that liquid solutions have a perfectly constant and definite resistance. The difficulties due to the polarization do not, in fact, prevent the conductivity from being determined with a continuous current,[1] but most experimenters have preferred to avoid polarization by employing an alternating current, in accordance with a method worked out by Kohlrausch. In an alternating current, the direction of the current changes very frequently, perhaps 50 to 50,000 times per second. If the frequency of alternation is high enough, the back E.M.F. does not become appreciable during any "half-period," and any minute polarization which may be set up during one half-period should be removed during the next half-period by the current passing in the opposite direction. For rough purposes, an ordinary cheap "buzzer-coil" is often used to provide the alternating current, although the frequency is generally not high enough to eliminate polarisation completely, and—what is still more serious—the alternating current generated is not quite symmetrical; for instance, the E.M.F. produced in one direction exceeds that produced in the other, and consequently the polarization caused during one half-period is not completely eliminated during the next. It is probable that even some of the classical work on conductivity has suffered through the employment of an unsuitable source of alternating current. Lately the use by Taylor and Acree [2] of a Vreeland oscillator giving a very symmetrical alternating current, with a frequency which can be varied at will, has led to very interesting results, and it is probable that the refined methods used by those experimenters have either eliminated, or allowed for, the many errors which are liable to arise in this class of work. It is impossible, however, to discuss the refinements of conductivity-measurement here; it is only possible to sketch the principles of the method as employed for ordinary work.

The solution to be tested is usually placed in a cell of a form similar to those shown in Figs. 66, 67 and 68. There are two electrodes E and F consisting of circular plates of platinum roughened by means of a sand-blast. Before the experiment, however, they must be covered with a velvety coating of "black platinum," by plating in a bath containing potassium platinichloride together with a small quantity of a lead salt;[1] this coating of black platinum is found to lead to more accurate and consistent results, probably because it greatly increases the active area of the electrodes. The electrodes are supported by platinum wires, which pass through the glass walls into the tubes G and H. When the apparatus is to be used, the tubes G and H are filled with mercury, and the ends of the conducting wires which are intended to join the cell to the rest of the apparatus require merely to be thrust down the tube in order to obtain a connection of very low resistance; the importance of avoiding appreciable resistance in the connections, where the resistance of a liquid is being measured, will be readily understood, and these "mercury contacts" are of great service for the purpose.

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[1] Methods of determining conductivity using a continuous current are described by F. W. Kohlrausch and L. Holborn, "Leitvermögen der Elektrolyten," (Teubner), and by E. Newbery, *Trans. Chem. Soc.* **113** (1918), 701.

[2] W. A. Taylor and S. F. Acree, *J. Amer. Chem. Soc.* **38** (1916), 2403, 2415.

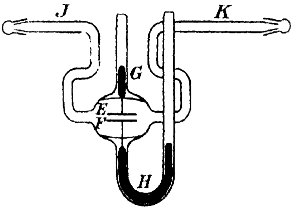

FIG. 66.—Conductivity Cell for Solutions of very low Conductivity.

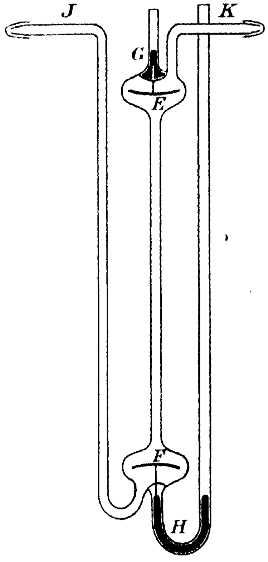

FIG. 67.—Conductivity Cell for Solutions of very high Conductivity.

The different forms of conductivity cell shown are useful for different purposes.[2] When a liquid of very low conductivity is to be tested, the electrodes must be large and close together, as in Fig. 66 ; when the conductivity of the liquid is high, the electrodes are farther apart, and, in extreme cases, the column of liquid between them is constricted by using the dumb-bell form of cell (Fig. 67). Both these types of cells are filled in the same manner as a pipette, the side tubes J and K being provided for the purpose. When the cell has been filled, the side tubes are closed by small caps. Fig. 68 shows a simple form of cell very convenient for rough work ; it has, however, the obvious disadvantage that the platinum plates, unless very thick and rigid, are liable to bend appreciably when lifted out of the cell and replaced, and a minute change in the distance between the electrodes may be produced, which will cause an error in the results.

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[1] Details of the method of "blackening" platinum electrodes will be found in A. Findlay's "Practical Physical Chemistry" (Longmans, Green), Chapter IX.

[2] E. W. Washburn, *J. Amer. Chem. Soc.* **38** (1916), 2431.

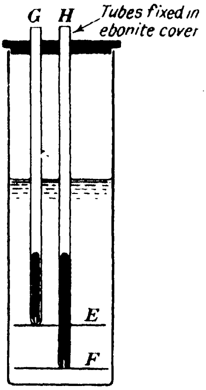


FIG. 68.—Conductivity Cell for Rough Work.

A telephone receiver is used as a delicate instrument to detect an alternating current ; quite a feeble alternating current passing through the coils of the receiver produces a vibration of the iron diaphragm, by alternately sucking it in and releasing it, and the vibration gives rise to a very audible "buzz."

The apparatus known as a Wheatstone Bridge, consisting in the simplest form of a stretched wire of high resistance and uniform thickness, capable of being tapped at any point by means of a sliding contact, is connected up with the rest of the apparatus in the method shown in Fig. 69. The conductivity cell is placed at R_1, and a standard coil of known resistance is placed at R_2 ; they are joined to one another and to the two ends of the stretched wire by stout conductors, the resistance of which can be neglected.

The coil or oscillator is then started, the receiver is raised to the ear, and the sliding-contact is adjusted until a position, X, is found at which there is no buzzing in the receiver. At that position, then, there is no current passing through the receiver, and the points X and Y must be at the same potential.

The current passing between the terminals P and Q of the coil or oscillator follows, between the points A and B, two different paths ; part of it passes along the stretched wire ; the rest passes through the resistances R_2 and R_1. The drop of potential over any portion of either path is proportional to the resistance of that portion ; therefore

$$\frac{\text{Resistance } R_2}{\text{Resistance } R_1} = \frac{\text{difference of potential between A and Y}}{\text{difference of potential between Y and B}}$$

Similarly, along the stretched wire,

$$\frac{\text{Resistance of Portion AX}}{\text{Resistance of Portion BX}} = \frac{\text{difference of potential between A and X}}{\text{difference of potential between X and B}}$$

But X and Y are at the same potential, and consequently,

difference of potential between A and Y = difference of potential between A and X, and

difference of potential between B and Y = difference of potential between B and X.

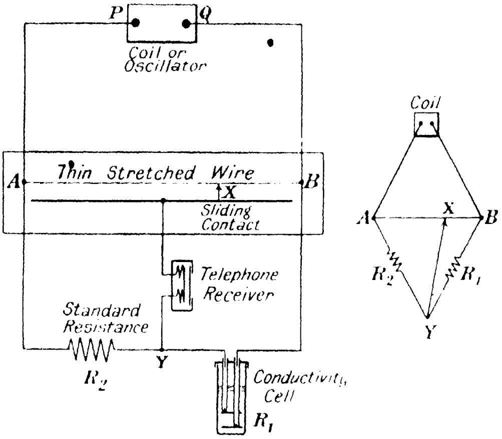


FIG. 69.—Measurement of Conductivity of an Electrolyte.

It follows that

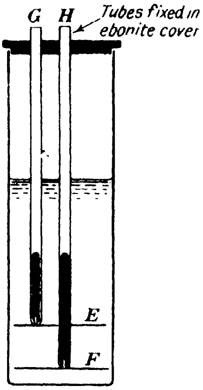
$$\frac{\text{Resistance } R_2}{\text{Resistance } R_1} = \frac{\text{Resistance of portion AX}}{\text{Resistance of portion BX}}$$

The stretched wire is uniform in cross-section, and the resistance of any part of it is proportional to the length; therefore

$$\frac{\text{Resistance } R_2}{\text{Resistance } R_1} = \frac{\text{length AX}}{\text{length BX}}$$

The lengths can easily be measured, and, the resistance R_2 being known, that of R_1 is easily calculated. Its reciprocal is the conductivity of the cell.

be tested, the electrodes must be large and close together, as in Fig. 66; when the conductivity of the liquid is high, the electrodes are farther apart, and, in extreme cases, the column of liquid between them is constricted by using the dumb-bell form of cell (Fig. 67). Both these types of cells are filled in the same manner as a pipette, the side tubes J and K being provided for the purpose. When the cell has been filled, the side tubes are closed by small caps. Fig. 68 shows a simple form of cell very convenient for rough work; it has, however, the obvious disadvantage that the platinum plates, unless very thick and rigid, are liable to bend appreciably when lifted out of the cell and replaced, and a minute change in the distance between the electrodes may be produced, which will cause an error in the results.



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The current passing between the terminals P and Q of the coil or oscillator follows, between the points A and B, two different paths; part of it passes along the stretched wire; the rest passes through the resistances R_2 and R_1. The drop of potential over any portion of either path is proportional to the resistance of that portion; therefore the purest water can be attributed to the fact that even water is split up—to a very small extent—into H˙ and OH′ ions.

A very interesting case is that of the five ammonia-compounds of platinic chloride ($PtCl_4$); it has been pointed out in the introduction that the chlorine atoms which form part of a stable "group of six," cannot break away to form chlorine ions. This is shown very clearly by the following values for the conductivity[1]:—

Compound.	**Molecular Conductivity.**
$PtCl_4 \cdot 6NH_3$ or $Pt[(NH_3)_6]Cl_4$	522·9
$PtCl_4 \cdot 5NH_3$ or $Pt\begin{bmatrix}(NH_3)_5 \\ Cl\end{bmatrix}Cl_3$	Unknown
$PtCl_4 \cdot 4NH_3$ or $Pt\begin{bmatrix}(NH_3)_4 \\ Cl_2\end{bmatrix}Cl_2$	228
$PtCl_4 \cdot 3NH_3$ or $Pt\begin{bmatrix}(NH_3)_3 \\ Cl_3\end{bmatrix}Cl$	96·75
$PtCl_4 \cdot 2NH_3$ or $Pt\begin{bmatrix}(NH_3)_2 \\ Cl_4\end{bmatrix}$	Very small

In ordinary salts, if the dissociation into ions is complete and the mobility of the ions remains constant, the conductivity should be proportional to the concentration. Normal potassium chloride, for instance, should have exactly ten times the conductivity of decinormal potassium chloride. To express the same fact in a different way, the **equivalent conductivity,** which may be defined as the

$$\frac{\text{Specific Conductivity of a Solution}}{\text{Number of Gram-equivalents present in 1 c.c.}}$$

should remain the same at all concentrations. Actual measurements show, however, that, although the equivalent conductivity tends to become constant at great dilution, in more concentrated solutions it falls below the maximum value. This is shown—in the case of potassium chloride and silver nitrate—by the table below,[2] which refers to a temperature of 18° C.

Concentration.	**Equivalent Conductivity.**	
Gram-equivalents per litre.	**Potassium Chloride.**	**Silver Nitrate.**
1·0	98·2	67·6
0·1	112·0	94·3
0·01	122·4	107·8
0·001	127·3	113·1
0·0001	129·0	115·0
Infinite dilution. Limiting value about	130·0	115·8

The numbers given in the last line show the limiting value to which the conductivity appears to approach closer and closer as the dilution increases.

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[1] A. Werner and A. Miolati, *Zeitsch. Phys. Chem.* **14** (1894), 510.

[2] A. A. Noyes and K. G. Falk, *J. Amer. Chem. Soc.* **34** (1912), 454. See also F. W. Kohlrausch and L. Holborn, "Leitvermögen der Elektrolyten" (Teubner), p. 159.

The falling off of equivalent conductivity at high concentrations is generally attributed to the fact that, since the ionization is not complete at high concentrations, there are actually less ions to carry the current. On the assumption that this is the only cause, it is possible to calculate the ionization of the salt at any concentration. For instance, the equivalent conductivity of silver nitrate at "infinite dilution" is about 115·8; that of silver nitrate solution of "normal" strength (i.e. containing one gram-equivalent per litre) is 67·6. Therefore, assuming that the mobility of the ions which do exist at normal strength is the same as at infinite dilution, the number of the ions must be only $\frac{67 \cdot 6}{115 \cdot 8} \times 100$, or 58·4 per cent. of the number at infinite dilution. In other words, the **percentage ionization** of silver nitrate in normal solution is 58·4 per cent.

The numbers obtained by this method should, however, be regarded as only approximate; there is no justification for assuming that the mobility of the individual ion remains unchanged; the increased viscosity of the concentrated solution, and the increased tendency for undissociated molecules to attach themselves to the ions will certainly cause an error. The effect of the varying viscosity is often allowed for in calculating the percentage ionization, but the effect of the other factor is less easy to estimate. Moreover, as will be explained in the next chapter, certain physicists consider that salts are—in a sense—"completely ionized" at all concentrations; and if this view is accepted, the numbers evidently cannot be held to represent the "percentage of ionized molecules," whatever other significance they may have. The majority of chemists, however, whilst agreeing that the "ionization values"—as calculated by the conductivity method—may be interpreted in more than one way, nevertheless consider that the numbers given by the method in most cases furnish a very fair idea of the degree to which the molecules are broken up into ions. It is consequently of interest to finish the chapter by giving a table showing the percentage ionization of some common acids, alkalis and salts, as calculated by the conductivity method.[1]

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[1] The numbers for the weaker acids are those of J. Walker and W. Cormack, *Trans. Chem. Soc.* **77** (1900), 5. The others are quoted from R. A. Lehfeldt's "Electrochemistry" (Longmans, Green), or calculated from numbers contained therein. A. A. Noyes and K. G. Falk, *J. Amer. Chem. Soc.* **34** (1912), 474, give a table showing the percentage ionization for numerous salts corrected for viscosity changes.

Percentage Ionization of some Common Compounds in N/10 Solution at 18° Centigrade

Compound.	Formula.	Percentage Ionization.
Acids.		
Hydrochloric acid	HCl	93·1
Nitric acid	HNO_3	93·3
Sulphuric acid	H_2SO_4	Approx. 60
Acetic acid	$CH_3{\cdot}COOH$	1·30
Carbonic acid	H_2CO_3	0·174
Hydrogen sulphide	H_2S	0·075
Hydrocyanic acid	HCN	0·011
Alkalis.		
Potassium hydroxide	KOH	91·0
Sodium hydroxide	$NaOH$	88·0
Barium hydroxide	$Ba(OH)_2$	79
Salts.		
Potassium chloride	KCl	85
Sodium chloride	$NaCl$	84
Sodium sulphate	Na_2SO_4	69
Barium chloride	$BaCl_2$	75
Zinc chloride	$ZnCl_2$	72
Magnesium sulphate	$MgSO_4$	42
Zinc sulphate	$ZnSO_4$	39
Copper sulphate	$CuSO_4$	38

Summary. The apparent passage of electricity through a salt solution is caused, not by a stream of electrons moving from cathode to anode, but by the movement of charged " ions " towards both electrodes. The " discharge " of the ions on the electrode involves decomposition of the dissolved salt ; often secondary reactions occur at the electrodes.

When the ions are coloured, their migration towards the electrodes can be observed experimentally. The movement of non-coloured ions can be followed by means of jelly containing a suitable indicator. The velocity is proportional to the potential gradient, and the rate of movement under unit potential gradient is called the " mobility " ; hydrogen is the most mobile of all ions.

According to Faraday's Law, one gram-equivalent weight of any metal should be deposited at the cathode (or dissolved at the anode) by 96,580 coulombs of electricity, assuming that the whole of the current is employed in depositing (or dissolving) the metal.

The conductivity of a solution is best measured by means of an alternating current and a Wheatstone Bridge, the solution being contained in a cell provided with blackened platinum electrodes. Specially pure water is desirable for accurate measurements of the conductivity of dilute solutions. Even absolutely pure water has a certain small conductivity, but ordinary laboratory water has a much higher conductivity, owing to the presence of dissolved substances. Solutions containing strong acids have high conductivity, owing to the great mobility of the hydrogen ion.

Assuming a salt to be wholly ionized and the mobility of the ions to be constant, the "equivalent conductivity" should be independent of the concentration. In practice, it falls off as the concentration rises, and from the values of the equivalent conductivity at any given concentration, a rough idea of the "percentage ionization" is arrived at.

CHAPTER VI

THE IONIZATION THEORY APPLIED TO THE CHEMICAL BEHAVIOUR OF SOLUTIONS

In the last chapter, the Ionization Theory was used to interpret, firstly, the movement produced in a solution by an electromotive force, and secondly, the simple connection between the amount of decomposition and the quantity of electricity which is expressed by Faraday's Law. For the explanation of those electrolytic phenomena it is not absolutely essential to imagine that the ions have a free existence before the current commences to pass, although it is simplest to assume that this is the case. In the present chapter, however, the Ionization Theory will be applied to interpret chemical reactions which have, at first sight, no connection with electricity. The application of the notion of ionization to pure chemistry is mainly due to Arrhenius, who based his arguments on the belief that the ions, such as Na˙ and Cl′, enjoy the same independence of motion in ordinary solutions as undissociated molecules. The success of the theory in explaining many of the facts of chemistry which otherwise would appear anomalous leads to the conclusion that the belief is justified; there appears to be little doubt that ions have a real existence in solutions to which no E.M.F. has ever been applied.

It may, however, be stated at once that the notion of free ions has aroused much opposition.* It has been pointed out that, whilst sodium and chlorine atoms are most highly reactive, their ions—if they are supposed to have a free existence in sodium chloride solutions—must be looked upon as stable and inert. The contrast between the properties of the uncharged atom and the charged ion is certainly most striking; the opponents of the Ionization Theory have been unwilling to regard the presence of an electric charge as sufficient cause for this remarkable change of properties.

The recent development of the electronic theory of the atom—if it has not entirely removed the objection—has at least given a simple interpretation of the change of properties caused by an electric charge. It is considered that the number of electrons surrounding the nucleus of the atom is equal to the atomic number. According to Langmuir,[1] these electrons are arranged around the positive nucleus, in spherical layers or "shells"; the outer layer is the one mainly concerned in determining the chemical reactivity of the atom. Now in the atoms of the inert gases, helion, neon, argon, krypton and xenon, which have no chemical reactivity, the outer layer must be complete, stable and self-sufficing. Consider then the elements, fluorine, chlorine, bromine and iodine, which come before the inert gases in the order of atomic numbers, and which therefore have one less electron in the outer shell. Here the atom is not stable but highly reactive; if, however, it absorbs one extra electron, the outer shell will become complete, and the resultant ion will possess a stability comparable to that of the inert gases. In other words, the ions (F′, Cl′, Br′ and I′) will belong to the "inert gas type."

Similarly, according to the ideas of Langmuir, the atoms of sodium, potassium, rubidium and caesium, which follow the inert gases, will have one electron outside the outermost complete shell; these atoms will therefore be reactive. But if the one "valency electron" is lost, the charged ion produced will now have a complete outer shell, and thus the positive ions (Na˙, K˙, Rb˙ and Cs˙) produced will be stable, belonging also to the "inert gas type."

Freezing-Point Determinations as Confirmation of the View of Independent Ions. The hypothesis of the existence of ions in solutions to which no electromotive force has ever been applied receives striking confirmation from the results of the determination of the freezing-points of dilute salt solutions. The depression of the freezing-point of a solvent through the presence of dissolved substances gives a means of arriving at the number of dissolved molecules present; in the cases of substances like sugar which do not conduct electricity the method has proved quite reliable for the determination of molecular weights. However, if the freezing-point of an aqueous solution of sodium chloride of known concentration is determined, it is found that the depression is nearly twice as great as that calculated on the assumption that the dissolved molecules are NaCl. If there are nearly twice as many molecules present, the fact can only be accounted for on the assumption that the majority of the molecules NaCl have broken up into halves, and it is natural to suppose that these halves are the ions Na˙ and Cl′.

Other salts, such as silver nitrate ($AgNO_3$) and potassium chloride (KCl), which would be expected to dissociate into two ions, also cause a depression of the freezing-point, which is nearly double the calculated quantity; the more dilute the solution, the more closely does the depression coincide with twice the calculated depression; this is evidently because the ionization becomes practically complete at high dilution. On the other hand, salts like sodium sulphate (Na_2SO_4) or calcium chloride ($CaCl_2$), which should form three ions, produce even greater depressions, which at high dilutions begin to approach three times the theoretical value.

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[1] I. Langmuir, *J. Amer. Chem. Soc.* **41** (1919), 868, 1543. See also the introduction to this volume, pages 25, 26.

The freezing-point method evidently gives a useful alternative method of calculating the percentage ionization of a solution, although it is not applicable to concentrated solutions. The results obtained confirm, on the whole, those arrived at from measurements of the conductivity. The agreement between the values for the ionization determined by the two methods is not indeed exact; considering the disturbing factors involved, that is scarcely to be expected. But no fair-minded person can consider the approximate agreement to be fortuitous, and the comparison of the "conductivity" and "freezing-point" values must be regarded as a sound argument in favour of the ionic dissociation theory.[1]

Application of the Law of Mass Action to Equilibrium between Ions and Molecules. Several important developments of the Ionization Theory were made possible by the application of the Law of Mass Action to the equilibrium between ions and undissociated molecules. Consider the equilibrium between the ions ($M^{\cdot}$ and X') and molecules of an imaginary salt MX,

$$M^{\cdot} + X' \rightleftharpoons MX.$$

When equilibrium is reached, the change

$$M^{\cdot} + X' = MX \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is clearly proceeding at the same rate as the opposing change

$$MX = M^{\cdot} + X' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now the velocity of change (1) is proportional to the concentrations (C_M and C_X) of the ions $M^{\cdot}$ and X'; it can be written

$$k_1 C_M C_X, \text{ where } k_1 \text{ is a constant.}$$

The velocity of the opposing change is proportional to the concentration of the undissociated molecules (C_{MX}) and can be written

$$k_2 C_{MX}, \text{ where } k_2 \text{ is a constant.}$$

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[1] The comparison between the numbers obtained by the two methods is discussed in W. C. D. Whetham's "Theory of Solution" (Cambridge University Press), Chapter XII.

are charged even in the gaseous state; the electrical forces acting between the positively charged sodium and the negatively charged chlorine serve to bind the atoms together. There is evidence[1] that in the solid state also the sodium and chlorine atoms retain their charge; no doubt it is the attraction between the charged sodium and chlorine atoms which keeps the atoms in their positions in the crystal-structure, and which affords to the crystal strength and rigidity. In the crystal-structure—as determined by the X-ray method—each sodium atom is surrounded by six chlorine atoms, and in view of the closeness of the oppositely charged atoms to one another, and the stability of the whole arrangement, it is fairly clear why the atoms, in spite of their charge, cannot move from their mean positions under the influence of an external E.M.F.; in other words, it is clear why crystalline sodium chloride possesses practically no electrical conductivity. When, however, the sodium chloride is dissolved in water, the state of affairs is different. If the solution is very dilute, the distance between the oppositely charged atoms becomes such that the attractive forces between them can be neglected in comparison with the force exerted by an external E.M.F. All the charged atoms are perfectly free to move towards either cathode or anode, according to their charge, without mutual hindrance, and we get a state of affairs corresponding to what we have hitherto styled "100 per cent. ionization." On the other hand, when the solution is concentrated, although the ions continue to move towards the electrodes under the influence of an E.M.F., yet their movement is, to some extent, modified owing to the attraction between oppositely charged ions. Indeed, in a very concentrated solution, we may picture two charged atoms occasionally coming so close together that their mutual attraction is very great compared to the effect of the applied E.M.F.; such a pair constitute for the moment a virtually "undissociated molecule," although the component atoms retain their charges.

We can picture, therefore, all possible gradations between absolutely free and independent "ions," existing in very dilute solution, and what are virtually "undissociated molecules" which will be met with only in very concentrated solutions. Clearly the equivalent conductivity of the solution will fall off gradually as the concentration rises, and the equivalent depression of the freezing-point—which depends on the number of units of solute having independent thermal movement—will likewise fall off with it. The whole of the atoms are charged at all dilutions, but the freedom of movement—or mobility—diminishes as the concentration rises.[1] According to this view, the numbers given in the table at the end of the last chapter—numbers which purport to represent the "percentage ionization" of various solutions—do not really show the "percentage of the molecules which are dissociated into entirely free ions"; but rather they serve as a measure of the mobility of the average ion, represented as a percentage of the mobility of the same ion as it exists in a very dilute solution.

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[1] P. Debye and P. Scherrer, *Phys. Zeitsch.* **90** (1918), 474. Compare M. Born, *Sitzungsber. Preuss. Akad.* (1918), 604.

As to whether the word "ion" should be used for those charged atoms which are scarcely free to move is a mere question of definition.[2] Some writers speak of the charged atoms of crystalline sodium chloride as "ions," although, strictly speaking, it is a misnomer to apply the word "ion" to cases where the charged atom is unable to move, since "ion" is derived from a Greek word meaning "to go."

If we accept the view that the atoms are charged at all concentrations, and that the "dissociation" is only restricted by the electric forces acting between the ions, it is quite easy to see why Ostwald's Dilution Law, which postulates an equilibrium between entirely free ions and absolutely undissociated molecules, must fail. Most of the recent attempts to replace it by some other law [3] which will explain the experimentally determined variations of the conductivity, and likewise of the lowering of the freezing-point, have not been entirely satisfactory. Some of the views advanced, although taking account of electrical interionic forces, nevertheless draw a sharp distinction between "free ions" and "bound ions" (i.e. those which possess too little kinetic energy to escape from the sphere of influence of one another); this sharp distinction appears to the present writer to be wrong. The complete quantitative solution of the problem is still awaited.

If the notion of "partially free ions" is a true one, then it is quite clear that the Law of Mass Action cannot be applied, with accuracy, to the equilibrium between molecules and free ions. But as a qualitative, or even a rough quantitative, guide to chemical phenomena, the law is useful; and it is legitimate to continue to distinguish between the states of an "undissociated molecule" and of a "free ion," although it should always be remembered that there may exist states intermediate in character between the two.

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[1] See the excellent paper by D. A. MacInnes, *J. Amer. Chem. Soc.* **43** (1921), 1217.

[2] W. D. Harkins, *Proc. Nat. Acad. Sci.* **6** (1920), 601, puts the position well.

[3] S. R. Milner, *Phil. Mag.* **23** (1912), 551; **25** (1913), 742; *Trans. Faraday Soc.* **15** (1919), i. 148; W. Hughes, *Phil. Mag.* **42** (1921), 134; J. C. Ghosh, *Trans. Chem. Soc.* **113** (1918), 449; H. Kallmann, *Zeitsch. Phys. Chem.* **98** (1921), 433. Compare the older views of W. Sutherland, *Phil. Mag.* **3** (1902), 161; **14** (1907), 1. A good criticism of Ghosh's theory is offered by J. Kendall, *J. Amer. Chem. Soc.* **44** (1922), 717.

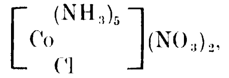
Application of the Ionization Theory to Precipitation. The precipitation of a sparingly soluble salt by the interaction of two soluble ones has been a familiar phenomenon since the days of the earliest chemists, but has only received a satisfactory interpretation with the advent of the Ionization Theory. There seems little doubt that the reactions between salt solutions are really reactions between ions; the precipitation of silver chloride caused by mixing solutions of sodium chloride and silver nitrate is often written,

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

But it is probably more correct to write it

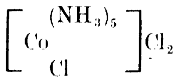
$$Ag^{\cdot} + Cl' = AgCl.$$

This view of precipitation is supported by the fact that the same precipitate is produced if any other ionizing silver salt be used instead of silver nitrate, or any other ionizing chloride be used instead of sodium chloride. On the other hand, chlorine compounds in which the chlorine does not exist as the ion Cl′, do not readily yield a precipitate of silver chloride with silver nitrate. The compound



$$\left[\mathrm{Co}\begin{array}{l}(\mathrm{NH_3})_5\\ \mathrm{Cl}\end{array}\right](\mathrm{NO_3})_2,$$

for instance, in which the chlorine forms part of a stable "group of six," gives no precipitate with silver nitrate at ordinary temperatures; the analogous salt



$$\left[\mathrm{Co}\begin{array}{l}(\mathrm{NH_3})_5\\ \mathrm{Cl}\end{array}\right]\mathrm{Cl_2}$$

has two-thirds of the chlorine precipitated by silver nitrate at ordinary temperatures; the remaining one-third is only precipitated on boiling.

In the majority of cases it is true to say that wherever there come together in solution two ions, the union of which would produce a salt of very low solubility, a precipitate of that salt will be formed. Nevertheless, there are many exceptions to the rule just given; for instance, an alkaline solution of calcium chloride yields with sodium phosphate a precipitate of calcium phosphate, whilst an acid solution yields no precipitate. Most heavy metals have sparingly soluble sulphides, but only a limited number are precipitated by hydrogen sulphide gas in the presence of a trace of acid.

These facts have long been known to analysts, who use them every day to detect, separate and estimate the different metals. Nevertheless, the average analytical chemist—when carrying out a precipitation—does not trouble himself with the theory of the process; he is content to follow closely the detailed instructions found in the practical books, which are founded upon the experience of others; and, if he happens to meet with a case where these methods fail, he is often at a loss to account for the failure, and seeks to avoid it by use of some "alternative method." The empirical character of the analytical methods is no doubt responsible for the fact that analysis is regarded as an unattractive branch of chemistry; as a matter of fact, the theory of analytical processes is full of interest.[1]

The application of the Ionization Theory has done much to throw light upon the apparent anomalies of precipitation processes. According to the statement of the case generally presented, when a solid salt stands in equilibrium with its saturated solution, the solid is regarded as being in equilibrium with the undissociated molecules, which in their turn are in equilibrium with the ions.

$$\text{Solid MX} \rightleftharpoons \text{Dissolved MX} \rightleftharpoons M^{\cdot} + X'.$$

It is no doubt more accurate to picture the equilibrium as a triangular one,[2]

$$\begin{tikzcd}
& \text{Dissolved MX} \arrow[dl, shift left] \arrow[dr, shift left] & \\
\text{Solid MX} \arrow[ur, shift left] \arrow[rr, shift left] & & M^{\cdot} + X'. \arrow[ul, shift left] \arrow[ll, shift left]
\end{tikzcd}$$

Those who assume that ionization is complete at all concentrations must regard the ions as in direct equilibrium with the solid salt

$$\text{Solid MX} \rightleftharpoons M^{\cdot} + X'.$$

For the sake of uniformity, the first of the three modes of thinking is here adopted. We shall assume that the equilibrium between ions and undissociated molecules in very dilute solution is given by the Law of Mass Action, although the failure of Ostwald's Law is a warning not to place much reliance on the quantitative accuracy of the results obtained in concentrated solutions. Experiments dealing directly with the solubility of salts [1] also show that the Law of Mass Action is not exactly obeyed, but for our present purposes it can be used as a rough guide.

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[1] The theory of analysis is explained in a most interesting manner in H. J. H. Fenton's "Notes on Qualitative Analysis" (Cambridge University Press), and also in Chapter XVI of the same author's "Outlines of Chemistry" (Cambridge University Press).

[2] J. Walker, *Brit. Assoc. Rep.* 81 (1911), 349.

When a solution containing a soluble silver salt is mixed with another containing a soluble chloride, the ions $Ag^{\cdot}$ and $Cl^{\prime}$, form a certain amount of undissociated AgCl molecules.

$$Ag^{\cdot} + Cl^{\prime} \rightleftharpoons AgCl.$$

Although the amount formed is very small, it usually exceeds the solubility limit of silver chloride—for the solubility limit of this particular salt is remarkably low—and the formation of the well-known precipitate commences, the undissociated molecules collecting at different points to form solid silver chloride. The equilibrium between ions and molecules is thus disturbed, and more ions combine together to form undissociated molecules. Precipitation thus proceeds until the concentration of ions is so small that they are in equilibrium with the minute concentration of undissociated AgCl molecules that can remain in the saturated solution :—

$$\text{Solid AgCl} \rightleftharpoons \text{Dissolved AgCl} \rightleftharpoons Ag^{\cdot} + Cl^{\prime}.$$

If, in this final state, when no more precipitation occurs, the concentrations of AgCl, $Ag^{\cdot}$ and $Cl^{\prime}$ be C_{AgCl}, $C_{Ag^{\cdot}}$ and $C_{Cl^{\prime}}$ respectively, we can write

$$C_{Ag^{\cdot}} \times C_{Cl^{\prime}} = K \times C_{AgCl}.$$

But at any given temperature, C_{AgCl} is constant, for it represents the solubility limit of silver chloride.

Therefore, $$C_{Ag^{\cdot}} \times C_{Cl^{\prime}} = \text{a constant}.$$

It follows that, by increasing the concentration of silver ions, we can decrease the quantity of chlorine ions remaining in the solution after precipitation. In other words, by adding a slight excess of silver salt to the chloride solution, the chlorine is precipitated even more completely than if only the theoretical quantity of silver salt is used. This is indeed a general rule in analysis; if complete precipitation is to be arrived at, a slight excess of precipitant should be employed; in fact, by using a slight excess of precipitant, it is sometimes possible to obtain almost complete precipitation, even where the solubility of the precipitate in pure water is by no means negligible. It should be noted, however, that in many cases—including that of silver chloride—the addition of a large excess of the precipitant may tend to redissolve the precipitate to some extent.

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[1] A. A. Noyes, W. C. Bray, C. R. Boggs, F. S. Farrell, M. A. Stewart and W. J. Winninghoff, *J. Amer. Chem. Soc.* 33 (1911), 1643, 1650, 1663, 1673.

Another phenomenon which is frequently quoted as an example of the same principle is the precipitation of sodium chloride by hydrogen chloride. A nearly saturated solution of sodium chloride is prepared; in this solution the sodium and chlorine ions are in equilibrium with a certain amount of NaCl molecules, but the solubility limit is not exceeded. The concentration (C_{NaCl}) of the undissociated molecules is given approximately by the equation

$$C_{\mathrm{NaCl}} = K \times C_{\mathrm{Na}^{\cdot}} \times C_{\mathrm{Cl}'}.$$

If now hydrogen chloride gas is passed into the liquid, the concentration ($C_{\mathrm{Cl}'}$) of chlorine ions is much increased; as a result the concentration of undissociated molecules (C_{NaCl}) is also increased, and the solubility limit is passed. A considerable quantity of sodium chloride is thereupon thrown down as a crystalline precipitate.

In general, we should expect a salt to be less soluble in a solution containing an ion in common with itself than in pure water. This is indeed usually found to be true. The solubility of silver acetate in water, for instance, is lessened by the presence either of silver nitrate or of sodium acetate.[1]

Another important effect of the reduction of ionization due to a "common ion" is the alteration in the precipitating powers of certain reagents. The aqueous solution of ammonia (NH_3) contains the hydroxide (NH_4OH) which behaves as a weak alkali, being dissociated thus

$$NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'.$$

If the salt ammonium chloride (NH_4Cl) is added to the solution, it largely increases the concentration of $NH_4^{\cdot}$ ions, and consequently aids the reaction in the "right to left" direction, whilst not correspondingly aiding the "left to right" change. As a result, ammonia containing ammonium chloride yields a smaller concentration of $(OH)'$ ions than ammonia without ammonium chloride, and behaves consequently as a weaker alkali. If, for instance, ammonia is added to a magnesium chloride solution, the concentration of $(OH)'$ ions is sufficient to precipitate magnesium hydroxide, $Mg(OH)_2$; but if ammonium chloride is present, no precipitate is produced.

Rather similar to the influence of ammonium chloride on ammonia is the effect of the presence of sodium acetate in reducing the ionization of acetic acid. When to a solution of acetic acid a little sodium acetate is added, the equilibrium

$$CH_3.COOH \rightleftharpoons CH_3.COO' + H^{\cdot}$$

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[1] W. Nernst, *Zeitsch. Phys. Chem.* 4 (1889), 372.

is shifted in the "right to left" sense owing to the excess of $(CH_3.COO)'$ ions; thus acetic acid behaves as a weaker acid in the presence of an acetate than in the absence of an acetate.

Another example which is of interest in analysis is the effect of acidity upon the ionization of hydrogen sulphide. A solution of hydrogen sulphide (H_2S) is a weak acid and contains the anions HS' and S'';

$$H_2S \rightleftharpoons HS' + H^{\cdot}$$
$$H_2S \rightleftharpoons S'' + 2H^{\cdot}$$

its precipitating power depends upon the presence of these anions. Now the presence of a strong acid, like hydrochloric, by greatly increasing the concentration of hydrogen ions present, shifts the equilibrium in the "right to left" direction, and so reduces the amount of $(HS)'$ and S'' ions present. Consequently only very sparingly soluble sulphides—such as those of mercury, lead, bismuth and copper—are precipitated by bubbling hydrogen sulphide through a salt solution containing hydrochloric acid. However, if the solution is acidified with a weaker acid, such as acetic acid in the presence of sodium acetate, other sulphides—rather more soluble than those just mentioned—are precipitated by hydrogen sulphide; zinc sulphide, for instance, is precipitated from a solution containing acetic acid, but dissolves again if warmed with a large excess of hydrochloric acid.

Other sulphides—such as manganese sulphide—are too soluble to be precipitated from an acetic acid solution, but are thrown down from a solution made alkaline with ammonia, for in such solutions the $(HS)'$ and S'' are still more plentiful. The precipitate of manganese sulphide is soluble in acids.

For similar reasons calcium oxalate can be thrown down on the addition of ammonium oxalate to an alkaline or neutral solution of calcium chloride, but not when the solution is acidified with hydrochloric acid; on the contrary, the precipitate of calcium oxalate readily dissolves in acids. Oxalic acid ($H_2C_2O_4$) is a rather weak acid and contains but few ions of the type $(C_2O_4)''$; on the other hand, ammonium oxalate is strongly ionized, and when $Ca^{\cdot\cdot}$ is present along with these ions, the solubility limit of calcium oxalate is usually passed, and the salt comes down as a precipitate.

In the systems of inorganic analysis commonly employed, advantage is taken of the difference in the solubilities of the hydroxides, sulphides and other salts to obtain an almost complete separation of the metals from one another.

Complex Ions. It has already been stated that the addition of a slight excess of the precipitant usually renders the precipitation more complete. There are, however, many noteworthy exceptions. If potassium cyanide is added to silver nitrate a white precipitate of silver cyanide, AgCN, is obtained, but if further potassium cyanide is added, the precipitate redissolves. The phenomenon is attributed to the formation of the complex salt $KCN.AgCN$ or $K[Ag(CN)_2]$, which ionizes into $K^{\cdot}$ and $[Ag(CN)_2]'$. The solution of this complex salt contains so few $Ag^{\cdot}$ ions that it gives no precipitate with sodium chloride. That the $Ag^{\cdot}$ ions are not entirely absent is shown by the fact that the liquid gives still a precipitate of silver sulphide when hydrogen sulphide is bubbled through the solution. Silver sulphide is even more insoluble than silver chloride, and requires a smaller concentration of $Ag^{\cdot}$ for precipitation. On electrolysis of the solution of the complex cyanide, it is found that the silver migrates—as a whole—towards the anode, instead of towards the cathode.

Many other metals form these complex cyanides, which do not show the reactions of the ordinary salts of the metals in question. For instance, the salts

Potassium cobalticyanide . . .	$K_3[Co(CN)_6]$
Potassium ferricyanide . . .	$K_3[Fe(CN)_6]$
Potassium ferrocyanide . . .	$K_4[Fe(CN)_6]$

fail to show the ordinary reactions of cobalt and iron salts.

Many of the insoluble sulphides—for instance, those of arsenic and antimony—dissolve in ammonium sulphide, forming soluble complex sulphides. There seems little doubt that small amount of complex ions exist in many solutions of ordinary double salts. A solution of carnallite, ($KCl.MgCl_2.6H_2O$) for instance, contains for the most part the simple ions $K^{\cdot}$, $Mg^{\cdot\cdot}$ and Cl'; but there is reason to think that in concentrated solutions the salt also exists to a small extent as $K^{\cdot}$ and $[MgCl_3]'$ ions.[1]

The effect of a "common ion" on the solubility of many sparingly soluble salts often points to the partial formation of complex ions even when the complex salt is not known in the solid state; silver chloride is practically insoluble in pure water or in dilute hydrochloric acid, but concentrated hydrochloric acid has a very appreciable solvent action on the salt. This suggests the partial formation of a soluble complex chloride,[2] possibly $H[AgCl_2]$. Silver chloride is also distinctly soluble in a strong solution of sodium chloride. The solubility of lead chloride is diminished by the presence of potassium chloride—as one would expect from the principle of Mass Action—and is apparently slightly reduced by a *small* addition of lead nitrate, but a *further* addition of lead nitrate increased the solubility.[1] This may point to a complex salt of the type $[PbCl]NO_3$.

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[1] R. Abegg and G. Bodländer, *Zeitsch. Anorg. Chem.* **20** (1899), 474.

[2] Compare E. H. Riesenfeld and H. Feld, *Zeitsch. Elektrochem.* **26** (1920), 286, who find that in such solutions silver moves to the anode.

Very interesting information regarding the existence of complex ions is given by the electrolysis of a solution. In a concentrated solution containing potassium iodide and cadmium iodide, it is found that the cadmium moves on electrolysis to the anode. Presumably, therefore, a complex salt is formed, such as K_2CdI_4,[2] which ionizes into

$$2K^{\cdot} \text{ and } [CdI_4]''.$$

Another view[3] is that the complex salt formed is $KCdI_3$ ionizing to

$$K^{\cdot} \text{ and } [CdI_3]'.$$

Whichever view is adopted, it is clear that the cadmium will move towards the anode when an E.M.F. is applied. When the solution is diluted, the movement towards the anode becomes less pronounced; it would appear therefore that the complex ions break up to some extent

$$[CdI_4]'' \quad 4I' + Cd^{\cdot\cdot}$$

and that the movement of the $Cd^{\cdot\cdot}$ towards the cathode partly compensates for the movement of $[CdI_4]''$ to the anode.

In the last chapter it was pointed out that in a concentrated solution of simple cadmium iodide the cadmium moves towards the anode. This was explained by the attachment of CdI_2 molecules to the iodine ions; if it is imagined that definite complex anions are formed in this way, this view is equivalent to regarding the apparently simple salt CdI_2 as a complex salt

$$Cd[CdI_4] \text{ or perhaps } Cd[CdI_3]_2.$$

In dilute solutions, the complex breaks up and cadmium moves towards the cathode.

Reference may also be made to the colour of cobalt salts.[4] Solutions of simple cobalt chloride are, at ordinary temperatures red. The red colour is apparently due to $Co^{\cdot\cdot}$ ions, for the red constituent—when the solution is electrolysed—moves towards the cathode. Solutions of cobalt chloride containing calcium chloride are, however, blue, and, on electrolysis, the blue constituent is found to move towards the anode. It is thought, therefore, that the blue solution contains a complex salt,

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[1] A. A. Noyes and W. C. Bray, *J. Amer. Chem. Soc.* **33** (1911), 1648.

[2] A. Jacques, "Complex Ions in Aqueous Solutions" (Longmans, Green) pp. 16, 17.

[3] J. W. McBain, *Zeitsch. Elektrochem.* **11** (1905), 215. See also R. G van Name and W. G. Brown, *Amer. J. Sci.* **44** (1917), 453.

[4] F. G. Donnan and H. Bassett, Junr., *Trans. Chem. Soc.* **81** (1902), 939

$CaCl_2.CoCl_2$ or $Ca[CoCl_4]$, yielding the ions $Ca^{\cdot\cdot}$ and $[CoCl_4]''$.

The blue colour is attributed to the complex anions containing cobalt. It is interesting to notice that the solutions of cobalt chloride containing zinc chloride are red, and that the red constituent moves—as usual—towards the cathode. Apparently in the double chloride of zinc and cobalt, it is the zinc, and not the cobalt, which enters the complex anion—a fact quite in keeping with the known tendency of zinc to take part in the formation of complexes. Thus, calcium cobalt chloride and zinc cobalt chloride are radically different:—

$CaCl_2.CoCl_2$ or $Ca[CoCl_4]$, ionizing into $Ca^{\cdot\cdot}$ and $[CoCl_4]''$ (blue)
$ZnCl_2.CoCl_2$ or $Co[ZnCl_4]$, ionizing into $[ZnCl_4]''$ and $Co^{\cdot\cdot}$ (red)

Character of the Precipitate. The character of the precipitate formed when two solutions are mixed depends on many factors. If the degree of super-saturation is very great, crystallization is likely to start at a very large number of points and a fine precipitate results; many of the practically "insoluble" substances, such as barium sulphate, are thus produced as very fine precipitates. On the other hand, when the degree of super-saturation is only moderate, crystallization will start at relatively few points and crystals of appreciable size are produced; sodium chloride—precipitated from a solution by hydrochloric acid—comes down as a visibly crystalline precipitate. Potassium platinicyanide—produced on mixing a solution of potassium chloride with a solution of platinum chloride—is another example of a crystalline precipitate. Both these salts have a solubility far greater than that of barium sulphate, and the degree of super-saturation produced at the moment of mixing is not very great.

In the precipitates of the comparatively soluble substances, which are produced comparatively slowly, a geometrical crystalline form of grain is often developed and can be observed if the precipitate is examined under the microscope. In other cases, crystal-skeletons and dendritic forms are produced. Where, however, the degree of super-saturation is great, and the precipitate is very fine, it is impossible to make out any definite crystalline form even under the most powerful microscope. Such precipitates are often referred to as "**amorphous.**"

It is, however, thought by some chemists—notably by von Weimarn—that the "amorphous grains" are really aggregates of minute crystalline particles. This point of view is supported by the following observations. When solutions of manganese sulphate and barium thiocyanate (two exceptionally soluble salts) are mixe together in very concentrated solutions, a gelatinous precipitate barium sulphate is obtained. From solutions of intermedia concentration, the familiar fine amorphous precipitate of bariu sulphate is thrown down. By using, however, more dilute solution star-shaped crystal-skeletons and needles are obtained, which ca be recognized by examining the precipitate under the microscope evidently, the effect of using more dilute solutions is to diminis the degree of super-saturation, and, the number of nuclei produce being smaller, the individual crystals attain a larger size. If t dilution is still further increased, the growth is slower, and t precipitate contains grains of well-marked geometrical outline—tha is to say, characteristic microscopic crystals. If the concentratio of the solutions is reduced below about N/7,000, no precipitate produced even after many years.[1]

Many other of the highly insoluble substances which are commonly produced as apparently structureless precipitates can obtained as crystals of a size visible to the naked eye when t reacting salts are allowed to come together very slowly in a dilut solution.[2]

Much more direct evidence of the crystalline character of appa ently amorphous precipitates has lately been afforded by t X-ray study of precipitated silver chloride and silver bromide ; has been shown that these precipitates consist of minute crystalli particles, which are too small for recognition under the microscop The atoms in each particle are found to be arranged on a cub lattice, the arrangement being the same as in silver bromide crysta prepared by the solidification of the fused salt.[3]

Reference may here be made to the **gelatinous precipitates**, which the hydroxides afford many examples. In outward appea ance, they would seem to be entirely structureless, but it is ve likely that here also we have to deal with aggregates of very sma particles, probably of a crystalline character. Apparently it is t most insoluble substances which tend to be thrown down i gelatinous form ; as has been stated above, barium sulphate ca be thrown down in a gelatinous form if very concentrated solutio are employed. Presumably the degree of super-saturation is i such cases very great, and the particles produced are very sma and very numerous. On account of the very small size of t primary particles, they readily link themselves to one another form secondary aggregates, and much water is included within the network of particles thus obtained. This causes the gelatinous character of the precipitate. The gelatinous state is further considered in the next chapter.

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[1] P. P. von Weimarn, *Koll. Zeitsch.* **3** (1908), 282. See also W. D. Bancrof *J. Phys. Chem.* **24** (1920), 100, who restates von Weimarn's views in a luc manner, discarding much that is open to criticism.

[2] See O. Lehmann, "Molekular Physik" (Engelmann, 1888), Vol. I, p. 51

[3] R. B. Wilsey, *Phil. Mag.* **42** (1921), 262.

Although von Weimarn is probably quite correct in saying that the ultimate particles of many apparently amorphous precipitates are crystalline, yet it seems very possible that truly amorphous precipitates may also exist, in which the ultimate particles can be regarded as drops of super-cooled liquid—or as globules of a glassy character.[1]

The so-called "**membrane**" **precipitates** deserve brief notice at this point. When a single drop of copper sulphate solution is cautiously introduced into the centre of a solution of potassium ferrocyanide, the drop becomes surrounded by a thin membrane of insoluble copper ferrocyanide, which keeps the copper sulphate within it from intermingling further with the solution outside, so that the drop remains separate from the rest of the liquid. This tenacious and apparently elastic skin seems to consist of particles of colloidal size and is threaded by channels of about 10–20 $\mu\mu$ diameter which are impermeable to the two reacting salts.[2] "Membrane precipitates" of a rather similar character are often seen when hydrogen sulphide gas is bubbled through the solution of the salt of a metal having an insoluble sulphide.

Often the very fine precipitates formed at the moment of the mixing of the precipitants rapidly become coarser. This is well seen in the case of silver chloride. When hydrochloric acid and silver nitrate are mixed, the particles of silver chloride are very small at first, but soon commence to adhere to one another, forming "clots" of considerable size. In many cases, the presence of small quantities of electrolytes in the solution have a marked effect upon the adhesion of the particles to one another; the factors involved are similar to those governing the flocculation of colloid solutions—a subject which is discussed in the next chapter.

Another well-known case of coarsening is that of barium sulphate. When first produced this precipitate is usually so fine as to pass through ordinary filter-paper. But if it is allowed to stand for some time in contact with hot water containing a trace of hydrochloric acid and ammonium chloride, the grain becomes coarser and the precipitate can no longer pass through filter-paper. This is usually attributed to the fact that the larger grains grow at the expense of the smaller ones. Experimental investigations have been carried out which are interpreted as showing that very small grains of barium sulphate are much more soluble than the larger grains.[1] A solution which is super-saturated with respect to the larger grains may yet be unsaturated with respect to the smaller grains. The small amount of hydrochloric acid present is supposed to have a partial solvent action on the barium sulphate; the smallest grains are mainly attacked, and, since the solution produced is super-saturated with respect to the large grains, deposition occurs on the large grains. This renders the solution again unsaturated with respect to the smaller grains, which are further attacked, and the process of the dissolution of the small grains accompanied by the growth of the big grains proceeds until all the small grains have disappeared.

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[1] W. D. Bancroft, "Applied Colloid Chemistry" (McGraw-Hill), 1921 edition, p. 166.

[2] F. Tinker, *Proc. Roy. Soc.* 92 [A] (1916), 357; *Trans. Faraday Soc.* **13** (1917), 133.

Recent work, however, would tend to show that this is not the main cause of the coarsening of barium sulphate, which is largely due to the fact that the fine particles first produced adhere together to form secondary aggregates.[2]

Evolution of Gases. Hitherto we have considered only the separation of solids; the chapter would be incomplete if some slight reference were not made to the separation of gases when their solubility limit is exceeded.

The principles which determine the evolution of a gas are essentially the same as those determining the precipitation of a solid. Carbon dioxide dissolves in water, yielding carbonic acid (H_2CO_3), which forms salts (the carbonates) with metallic oxides; but carbonic acid is a weak acid, and the solubility of carbon dioxide is small. Therefore on the addition of a strong acid to a solution of a carbonate, carbon dioxide gas is evolved. It is not evolved, however, by acids like hydrocyanic, which are very much weaker than carbonic; on the contrary, carbon dioxide will slowly expel hydrocyanic acid from the cyanides.

Even strong and soluble acids, like nitric and hydrochloric, are evolved—owing to their volatility—when nitrates and chlorides are heated with the less volatile acid, sulphuric acid; thus nitrates and chlorides can be converted into sulphates. The change is important both in industry and in analysis.

But even sulphuric acid (or the anhydride, SO_3) is volatile at a higher temperature, and by heating a sulphate with the non-volatile boron oxide (B_2O_3), it is possible to expel the sulphuric anhydride, and convert the sulphate into a borate. This is an interesting change because it represents an example of a rare phenomenon—the expulsion of a fairly strong acid (sulphuric) by a weak one (boric); it is rendered possible only by the non-volatility of the latter.

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[1] G. A. Hulett, *Zeitsch. Phys. Chem.* **37** (1901), 385; W. Ostwald, *Zeitsch. Phys. Chem.* **34** (1900), 503. The quantitative conclusions of these writers are not universally accepted at the present time.

[2] Sven Odén; Svensk Kem. Tidskr. **32** (1920), 108; Abstract, *Chem. Zentralblatt,* **91** (1920), iii. 705.

Summary. The hypothesis of the independent existence of charged ions in ordinary solutions leads to a rational explanation of many peculiar facts concerning the precipitation and dissolution of sparingly soluble salts. The hypothesis is supported by the abnormally low values for the lowering of the freezing-point of water by salts. The application of the Law of Mass Action to the equilibrium between ions and unionized molecules leads us to expect that the expression $\frac{a^2}{Y(1-a)}$ should be constant for a given binary salt at all dilutions. For weak acids and alkalis this is found to be true, but for salts, except at extremely great dilution, it is far from true. The failure of "Ostwald's Dilution Law"—as it is called—is best explained by the assumption that it is impossible to draw a sharp line of distinction between "free ions" and "undissociated molecules." The atoms are charged at all dilutions, but the attraction between oppositely charged ions—even at a distance—causes some restraint on their relative motion: probably the so-called "undissociated molecule" is merely an extreme example of the same sort of restraint.

Nevertheless the notion of ionization can be applied qualitatively with great success to explain the various reactions used in analysis. It explains, for instance, why an insoluble salt is rendered less soluble by the presence of a common ion in solution; why ammonia is rendered a weaker alkali by the presence of ammonium chloride, and acetic acid a weaker acid by the presence of sodium acetate; why sulphuretted hydrogen will only precipitate metals with exceptionally insoluble sulphides from acid solution, but will precipitate other metals from alkaline solution; and, lastly, why calcium oxalate can be thrown down from ammoniacal solution, but dissolves in hydrochloric acid.

Often, however, a precipitate redissolves in excess of the precipitant, and this is attributed to the formation of complex anions. The explanation can in many cases be verified by the migration of the heavy metal towards the anode—instead of the cathode—when the solution is electrolysed.

The character of the precipitate produced depends on the degree of super-saturation. Comparatively soluble salts like potassium platinichloride come down as crystalline precipitates. More insoluble substances, like barium sulphate, are commonly thrown down in a form that is apparently amorphous—sometimes even gelatinous. From more dilute solutions, however, the same salts are produced as crystalline precipitates, and it is reasonable to suppose that many of the so-called amorphous precipitates are really aggregates of extremely fine crystals.

CHAPTER VII

THE COLLOIDAL STATE IN METALS AND METALLIC COMPOUNDS

In the last chapter, reasons have been given for thinking that in the ordinary solutions of metallic compounds, the particles of solute are for the most part electrically charged; in instances where there is little dissociation into electrified ions—as in the case of the hydroxides of the heavy metals—the solubility is usually very small. In the present chapter, it will be shown that many substances which, under normal conditions, are nearly insoluble in water, can nevertheless be obtained in a state of "**colloida solution,**" and that the particles existing in these colloidal solutions are also electrically charged. Moreover, the electrification appears to be essential for the stability of the system because, if the charge be removed, precipitation of the dissolved substance nearly always occurs.

Colloidal solutions are referred to by many writers as "**sols**" where the "dispersion medium"—the solvent or liquid throughou which the colloid particles are dispersed—is water, the colloida solution is referred to as a "**hydrosol.**"

The colloidal solutions of solid substances which under ordinary circumstances are nearly insoluble, may be regarded as suspension of the substances in particles of such small size that they ar indistinguishable to the eye, and fail to settle, remaining suspended in the liquid indefinitely; they may conveniently be called "**suspensoids.**" There is another class of materials, however which form colloidal solutions; these include complex organi substances like gum and gelatine. The ordinary solution of gelatin contains particles of colloidal size, and the solution has many of th properties of the suspensoid sols referred to above. It appear permissible in such a liquid to identify the colloid particles with th molecules of gelatine,[1] and to ascribe the fact that a gelatine solution possesses colloidal properties to the fact that gelatin consists of extremely large complex molecules; many chemists however, consider this a wrong view, and regard the colloid particles of a gelatine sol as aggregates of molecules. There is no need to enter into this controversy, which has been caused mainly by different conceptions of what the word "molecule" means. It is enough to point out that colloidal solutions of these complex bodies possess certain properties rather different from those of the suspensoid colloids referred to above; they seem to resemble emulsions (i.e. systems consisting of drops of one liquid suspended in another), rather than suspensions of solid bodies, and they are therefore termed "**emulsoids.**" The colloid solutions of emulsoids differ from those of suspensoids in being viscous and in general more stable; when they suffer change, the emulsoids tend to "gelatinize," whilst, in a suspensoid sol, the particles tend to aggregate together to form a precipitate which settles to the bottom of the liquid.

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[1] Compare J. Loeb and R. F. Loeb, *J. Gen. Physiol.* 4 (1921), 187; especiall pages 209, 210.

But, although the terms "suspensoid" and "emulsoid" are convenient, it is a mistake to regard it as certain that the so-called suspensoid sols consist of solid particles in a liquid, whilst the so-called emulsoid sols consist of liquid globules in another liquid. It appears to the present writer that the sharp distinction between solids and liquids may not be maintained in reference to particles of sizes comparable to that of a molecule. In any case, the fact that a sol has a high viscosity cannot be taken as a certain proof of an emulsoid character. The viscosity depends on many factors; for instance, sols containing small particles have usually a much higher viscosity than similar sols consisting of large particles.[1] There appear to be cases of colloids possessing transitional properties between those of suspensoids and emulsoids.

It was stated in the introduction that colloidal solutions differ from ordinary solutions mainly in the size of the particles. The colloidal solution of a suspensoid is intermediate in character between a true solution on the one hand and a true suspension on the other. There is probably no sharp line of division between the three classes. The following table, which gives the diameter of the particles occurring in the various cases, illustrates the transition from one type to the other.[2]

Ordinary Molecular size :—

Hydrogen molecule	$0{\cdot}1\mu\mu$	·0000001 mm.
Water molecule	$0{\cdot}13\mu\mu$	·00000013 mm.
Sodium chloride molecule	$0{\cdot}26\mu\mu$	·00000026 mm.
Chloroform molecule	$0{\cdot}8\mu\mu$	·0000008 mm.

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[1] Th. Svedberg, *Trans. Faraday Soc.* **16** (1921), Appendix, pp. 7, 8.

[2] Partly taken from W. Ostwald, "Handbook of Colloid Chemistry": translation by M. H. Fischer, with notes by E. Hatschek (Churchill, 1919), pp. 30, 31.

Colloidal size :—		
Gold colloid particle	2 to $15\mu\mu$	= ·000002 to ·000015 mm.
Starch " molecule "	$5\mu\mu$	= ·000005 mm.
Precipitated gold particle	$75\mu\mu$	= ·000075 mm.
Particles in Suspensions and Emulsions :—		
Mastic suspension, particle	$0{\cdot}5$ to 1μ	= ·0005 to ·001 mm.
Kaolin particles (china clay)	1μ to 3μ	= ·001 to ·003 mm.
Globules of fat in milk	2μ to 10μ	= ·002 to ·01 mm.

(*Note.*—$1\mu\mu$ = ·000001 mm. ; 1μ = ·001 mm.)

A special interest attaches to colloidal solutions owing to the fact that the particles are large enough to be detected by means of the ultra-microscope, and yet small enough to show appreciably the motion, known as " Brownian Movement," which indicates the thermal agitation existing in a solution. Whereas, in the study of ordinary solutions, we can merely watch the combined effect of the movement of millions of molecules or ions, it is possible—in colloidal solutions—to observe the motion of the individual particles.

The details of the design of the **ultra-microscope**, as developed by Zsigmondy and Siedentopf, must be sought elsewhere.[1] The principle, however, is simple enough. In the ordinary forms of microscope—as opposed to the ultra-microscope—the objects are viewed by *transmitted* light. An opaque particle will therefore appear black against a light background. It is found, however, that very small particles cannot be detected at all by transmitted light, since the minute blocking out of light due to any one tiny particle will be inappreciable to the eye, owing to the vastly greater amount of light which still reaches the eye from points all round the particle. If, however, the arrangement of the microscope is such that none of the light used for the illumination can enter the microscope tube unless it is deflected from its normal course by striking on some suspended body, then we may hope to see any minute particles suspended in a transparent liquid, as light points on an absolutely black background. So long as the illumination is very bright, and the power of the microscope high, it will be possible to detect and count particles of very minute size, although no direct information regarding the size or shape is thereby afforded. Such is the principle of the ultra-microscope.

In Fig. 70 is shown, diagrammatically, the essential difference in the principles of the ordinary microscope (A) and the ultra-microscope (B). In A the liquid L is illuminated from below, and the suspended particles, when seen from above, will appear black against a white background (if indeed they are visible at all). In B the liquid is illuminated from the side, and the suspended particles appear white against a dark background.

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[1] R. Zsigmondy, " Colloids and the Ultra-Microscope," translation by J. Alexander (Wiley) ; R. Zsigmondy, " Kolloid Chemie " (Spamer) ; E. F. Burton, " Physical Properties of Colloidal Solutions " (Longmans, Green).

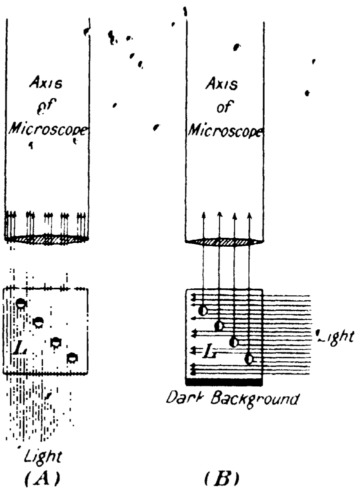

Fig. 70.—The Essential Difference between (A) the Ordinary Microscope, (B) the Ultra-Microscope.

The matter is made even clearer by an example familiar to all. If a beam of sunlight is allowed to enter a darkened room through an aperture in the shutters, the particles of dust suspended in the air along the path of the beam appear brightly illuminated, provided that they are viewed from the side, so that they "show up" against the dark walls of the room. It is due to this fact that the "path" of the light-rays through the air is visible; if the air was free from dust, the "path" of the light would not be detectable by the eye at all. Now, if instead of viewing the path of the light from the side, the eye is placed in the beam itself, no dust-particles are seen; the eye is merely dazzled with the intense general illumination which reaches it.

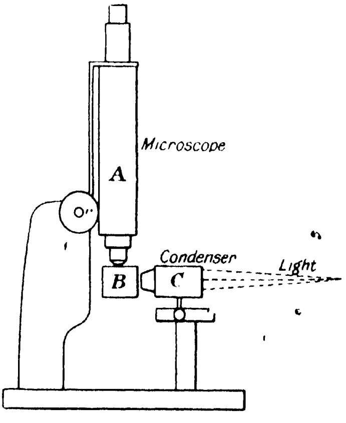

Fig. 71.—The Ultra-Microscope.

In the place of the dusty air, we can substitute a glass jar containing a colloidal solution. If this is viewed by transmitted light, it appears to be transparent; if, however, it is viewed from the side so that only light deflected in its direct course by striking the colloid particles can reach the eye, a turbidity can be detected. And if, further, the naked eye is aided by a high-power microscope, placed at right angles to the direction of the light, the individual particles which are responsible for the scattering or deflection of the light may perhaps be made out—provided the illumination is sufficient—and will then appear as bright points dancing upon a black background. In Fig. 71 light from an intense source (provided for instance by a pointolite lamp) is directed by means of the condenser C upon the colloidal solution placed at B, which is examined by a microscope A placed at right angles to the direction of the light; by an arrangement of this kind the individual colloid particles can be observed.

The older forms of ultra-microscope enable the observer to count particles as small as $5\mu\mu$, but the newer form of "immersion" ultra-microscope, which has much more intense illumination, allows them to be counted down to $3\mu\mu$, whilst it detects particles of even smaller sizes.[1]

The "**Brownian Movement**" of the particles, as seen when a colloidal solution is observed in the ultra-microscope, is most interesting. If, for example, a solution of gamboge or caoutchouc is studied, the particles will be seen darting about in haphazard fashion, and frequently changing their direction. Various observers have studied the course followed by individual colloid particles, one experimenter using the principle of the cinematograph for the purpose.[2] All observations indicate that the path followed by an individual particle is of an irregular zigzag character; the irregular and haphazard motion is usually ascribed to the fact that the chance impacts of the liquid molecules on one side of the particle may, at a given moment, happen to exceed those on the other side, whilst at the next moment, the state of affairs may be reversed. Careful research has shown that the visible movement of the colloid particles is governed by just the same laws as appear to govern the movements of the invisible molecules of gases and liquids, and it is possible to regard the Brownian Movement as an ocular demonstration of the correctness of the kinetic theory of gases and liquids.[3]

The Brownian Movement, as would be expected from kinetic considerations, falls off as the particles increase in size. The fat particles in milk exhibit it to a small extent, whilst particles larger than about 3–5μ do not show Brownian Movement at all. Evidently it is the Brownian Movement which prevents the particles from settling under the influence of gravity, for where the particles in suspensions and in emulsions are too large to show violent movement, gradual settling of the particles takes place. In a suspension of kaolin, the particles slowly sink to the bottom if the liquid is left unstirred; in milk, where the particles are lighter than the liquid in which they are suspended, the fat—or cream—gradually collects on the surface.

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[1] G. King, *J. Soc. Chem. Ind.* **38** (1919), 6T. The instrument is described by R. Zsigmondy, *Phys. Zeitsch.* **14** (1913), 975.

[2] V. Henri, *Comptes Rend.* **147** (1908), 62.

[3] J. Perrin, *Comptes Rend.* **146** (1908), 967. See also J. Perrin's excellent book, "Les Atomes" (Alcan).

Another property which gradually varies as the size of the particles changes is the power of passing through a porous material. The ordinary molecules and ions of salts will diffuse readily through ordinary parchment paper, whilst the larger particles of a colloidal solution fail to pass through. This is the basis of a method known as **dialysis**, which allows us to separate ordinary salts from colloidal substances. If a solution containing ordinary salts and also colloid particles is placed in a parchment "thimble" surrounded by pure water which is periodically renewed, the salts gradually pass through the parchment and are removed, leaving a pure colloid solution behind. The difference in permeability varies, however, gradually with the size of the particles, and by selecting a medium of the proper porosity, the separation of the larger from the smaller colloid particles is possible. Ordinary filter-paper prevents the passage of particles exceeding 5μ in size, whilst special "hardened" filter-paper holds all those larger than 2μ; clay cylinders are impervious to particles exceeding 0·4 to $0{\cdot}2\mu$, and special membranes are manufactured to stop the passage of still smaller particles. Upon this principle a system of **Ultra-filtration** has been worked out, for the separation of colloids from one another.[1] If a solution containing the organic dye, benzo-purpurin, and the inorganic colouring matter, Prussian Blue, is forced through a membrane filter of suitable porosity, the Prussian Blue is retained and the benzo-purpurin passes through.[2] The benzo-purpurin solution thus obtained can be forced through a still finer membrane, which retains the particles of the dye; the liquid which comes through this second membrane is colourless.

Cataphoresis. If two electrodes are immersed in a colloidal solution and an E.M.F. is applied to them, the particles commence to move either towards the cathode or towards the anode; this phenomenon, which is known as cataphoresis, shows that the particles are either positively or negatively electrified. Since the presence of colloid particles usually confers a distinct colour upon the medium in which they are suspended, the migration of the particles towards the electrode can be observed by methods similar to those described for coloured ions in a previous chapter.[1] The mobilities of colloid particles have been measured, and are of the same order of magnitude as those of ions. For instance, the mobility of the negatively charged particles present in a colloidal solution of silver varies between ·0002 and ·0004 cms. per sec., whilst that of the positively charged silver ion present in the solution of a silver salt is ·00049 cms. per sec.

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[1] H. Bechhold, *Zeitsch. Phys. Chem.* **60** (1907), 257; **64** (1908), 328.

[2] R. Zsigmondy and W. Bachmann, *Zeitsch. Anorg. Chem.* **103** (1918), 119.

It is interesting to observe that a fine suspension of clay particles in water exhibits cataphoresis; the particles wander to the anode when an E.M.F. is applied. Likewise, if an E.M.F. is applied to an emulsion of oil and water, the drops of oil usually move towards the anode, which shows that they also possess a negative charge.

It is most important, however, to notice that the sign of the charge can often be changed through the addition of acids, alkalis or salts to the liquid. For instance, in a colloidal solution of egg-albumin, which has previously been boiled, the particles move to the cathode in the presence of a trace of acid, but to the anode in the presence of a trace of alkali.[2] Evidently, therefore, the particles have a positive charge in acid solutions, and a negative charge in alkaline solutions. A similar change of direction is noticed in a solution of gelatine.

In such cases, it should be possible by adding just the right quantity of acid or alkali, to obtain a state in which the colloid particles move neither to the anode or cathode. It is always found, however, that as this point of electrical neutrality—which is known as the **iso-electric point**—is approached from either side, the colloidal solution becomes unstable, and a flocculent precipitate of the colloid substance appears in it. Since it seems—in most cases—impossible to keep a substance in colloidal solution under conditions which deprive the particles of their charge, it is natural to conclude that it is the repulsion caused by the electric charges on the particles which is the determining factor in preventing the particles from clustering together to form the "flocks" or "aggregates" that would constitute an ordinary precipitate. According to this view, when the charge is removed, the thermal agitation of the particles is, by itself, insufficient to prevent the union of the particles, and in consequence, precipitation occurs. Many authorities,[1] however, consider this simple explanation as scarcely sufficient, although undoubtedly it contains an element of the truth.[2]

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[1] Where the colloidal substance does not of itself possess sufficient colour, an indicator can be used. Thus a trace of ferric chloride will serve to show up the penetration of tannin into gelatinous matter under the influence of an electric current. See E. K. Rideal and U. R. Evans, *J. Soc. Chem. Ind.* **32** (1913), 633.

[2] W. B. Hardy, *Proc. Roy. Soc.* **66** (1900), 110; *J. Physiol.* **24** (1899), 288.

Experiments have been made which appear to show that it is not necessary to deprive the particles wholly of their charge in order to cause precipitation, but that when the potential difference between the colloid and the medium is reduced below a certain value, the particles begin to join together to form aggregates and this process continues until a visible precipitate appears.[3]

In many cases, the addition of a salt is capable of bringing about a reversal of the charge. The presence of aluminium salts are especially potent in converting negative colloids into positive colloids. The particles of a colloidal solution of gold or of silver normally move towards the anode, but the addition of the merest trace of an aluminium salt reduces the velocity very much, whilst addition of further small quantities cause the particles to move towards the cathode.[4]

Even in the case of an emulsion consisting of globules of oil suspended in water, the sign of the charge can be changed by the addition of aluminium chloride to the water. Under ordinary circumstances, as stated above, the oil-particles wander to the anode; but in the presence of aluminium chloride, they move to the cathode.[5]

The sign of a colloid is in several cases dependent on the manner in which the solution has been prepared. A colloidal solution of ferric hydroxide, for instance, can be produced by two distinct methods. In the first method, it is obtained by the hydrolysis of ferric chloride according to the equation,

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[1] See for instance W. C. McC. Lewis, *J. Soc. Chem. Ind.* **38** (1919), 4T, who says, "The difficulty of accepting this very simple view lies in the fact that peptization and protection—which depend upon adsorptive effects—occur between particles of the same electric sign, and therefore presumably repelling one another. I must confess to be not altogether satisfied with the view." Compare L. F. Knapp, *Trans. Faraday Soc.* **17** (1922), 457.

[2] The personal view of the present writer is as follows. At the interface between the colloid and the liquid, forces of electrical origin exist. Those acting *along* the interface (the interfacial tension) rise whenever those acting *across* the interface (the "adhesive forces" binding the colloid and liquid together) fall, and vice versa. At or near the iso-electric point, the interfacial tension is known to be a maximum, and accordingly the forces binding the colloid particles to the liquid are a minimum near the same point; hence colloidal solutions have a minimum stability at or near the iso-electric point. It is noteworthy that not only peptization, but also swelling, is at a minimum at the iso-electric point.

[3] F. Powis, *Trans. Chem. Soc.* **109** (1916), 734; R. S. Willows, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 101; R. Zsigmondy, *Zeitsch. Elektrochem.* **23** (1917), 148.

[4] E. F. Burton, *Phil. Mag.* **12** (1906), 472.

[5] F. Powis, *Zeitsch. Phys. Chem.* **89** (1915), 91.

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl,$$

the hydrochloric acid produced by the change being removed by continued dialysis; in the colloidal solution of ferric hydroxide thus prepared, the particles have a **positive** charge. In the second method, by slowly running in a $\frac{N}{100}$ solution of ferric chloride into slight excess of $\frac{N}{100}$ solution of sodium hydroxide—with constant shaking so that the alkali remains in excess at all points—a colloidal solution is prepared in which the particles have a **negative** charge.[1] The essential difference between the two methods of preparation is that, in the first method, ferric salts are present in excess all the time, whilst in the second method, sodium hydroxide is present in excess. All the circumstances go to prove that the ferric hydroxide particles prepared by the first method contain "adsorbed" ferric ions, and that the positive charge of the particles is due to these ferric ions; on the other hand, the ferric hydroxide produced by the second method have adsorbed hydroxyl ions, and in consequence the particles possess a negative charge.

It should be pointed out that if dialysis of the solution prepared by the first method is pushed so far that practically all the ferric chloride is removed from the solution, it becomes very unstable, and readily deposits a precipitate; this gives considerable support to the view that the charge is due to adsorbed ions. Similarly the negative form of ferric hydroxide is rendered unstable, if an attempt is made to remove the whole of the sodium hydroxide by dialysis.

Since the presence of ferric chloride is necessary for the stability of the colloidal solution produced by the first method, it is possible to look upon the whole as a complex salt of indefinite composition,

$$xFe(OH)_3.yFeCl_3$$

which is dissociated into the ions

$$xFe(OH)_3.yFe^{\cdots} \text{ and } 3yCl'.$$

From this standpoint, the colloidal particle is really an ion, although an ion of unusual size and of variable composition.

The notion of the colloid particle as an ion of a complex salt has rather special interest, as it reconciles two apparently diverse views which have been put forward by different authorities. It has long been known that precipitated ferric hydroxide when shaken up with ferric chloride solution passes—or appears to pass—

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[1] F. Powis, *Trans. Chem. Soc.* **107** **(1915)**, **818.**

into solution. Some chemists [1] hold that the phenomenon is due to the formation of a soluble basic chloride. Others [2] hold that there is no true solution at all, but only "peptization," the breaking up of the ferric hydroxide into colloid particles, which remain in suspension in the liquid, the peptization being brought about by the adsorption of ferric ions. If the colloid particles are regarded as the ions of a complex basic salt, the second view becomes practically identical with the first. It is necessary, however, to modify the first view by stipulating that the so-called "basic salt" shall have a composition which varies indefinitely with the amount of ferric chloride present. It is also necessary to point out that, owing to the large size of the colloid particles, the ferric hydroxide can be separated from the liquid by filtration through a suitable medium; in fact, under certain conditions, part of the hydroxide may even settle spontaneously to the bottom of the vessel under the influence of gravity.

An analogous case is the peptization of precipitated stannic acid by sodium hydroxide.[3] By treating the precipitate with different quantities of sodium hydroxide, we can get a colloidal solution containing particles of almost any desired size. If the sodium hydroxide is present in small amount, the particles are big, and the solution unstable; as the amount of alkali added is gradually increased, the average size of the particles becomes gradually smaller and the solution becomes more stable, until when the sodium hydroxide is present in very large amount, the particles are mostly of molecular size, and the solution can be regarded as a solution of sodium stannate, $\mathrm{Na_2Sn(OH)_6}$. We can regard the whole series as consisting of the salt

$$x\mathrm{NaOH}.y\mathrm{Sn(OH)}_4,$$

ionizing into

$$x\mathrm{Na}^{\cdot} \text{ and } x\mathrm{OH}'.y(\mathrm{Sn(OH)}_4),$$

the anion being, of course, the negatively charged colloid particle.

Somewhat similar is the case of the solutions of the "soaps," such as sodium oleate, sodium palmitate or sodium stearate. These substances dissolve readily enough in water, as is well known, but the presence of particles of colloidal size in the liquid can often be inferred from the fact that the solutions, even when prepared with distilled water, are distinctly turbid. Our knowledge of the nature of the colloid particles is largely due to the work of McBain.[1] It is found that, in concentrated solutions, the conductivity is considerable, but that the "molecular weight" of the solute—as found by a "dew-point method" (based on the same principle as the "boiling-point method" in general application)—is very high. This high molecular weight would lead one to suppose that the concentration of "ions" present in the solution is comparatively small, and we can only account for the high conductivity if we assume that each "ion" carries a large number of electric charges. These and other considerations led to the postulation of "ionic micelle theory" of soap solutions.

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[1] W. Pauli and J. Matula, *Koll. Zeitsch.* **21** (1917), 49; W. Pauli, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 14.

[2] For instance, H. B. Weiser, *J. Phys. Chem.* **24** (1920), 277, especially p. 285. Compare W. D. Bancroft, *J. Phys. Chem.* **20** (1916), 85.

[3] Compare the views of R. Zsigmondy, *Zeitsch. Anorg. Chem.* **89** (1914), 210, with those of W. Pauli, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 17. Zsigmondy, it should be noticed, considers that the effect of small additions of alkali is to break down the large secondary aggregates into primary colloid particles, but that excess of alkali causes further diminution of size through chemical action (stannate formation)—a process which, he says, "has nothing to do with peptization."

Consider the case of sodium palmitate, which we may write NaP, where P represents the group $C_{16}H_{31}O_2$. In moderately dilute solutions, below $\frac{N}{10}$, this is ionized in the ordinary way to $Na^{\cdot}$ and P'; where the solution is very dilute, partial hydrolysis also occurs, causing an alkaline reaction. On the other hand, in concentrated solutions $\left(N \text{ or } \frac{N}{2}\right)$, "micelles" are formed by the union of anions with undissociated molecules of the salt and possibly with water molecules also. Thus, in a concentrated solution, $n + x$ molecules of sodium palmitate may ionize to

$$n\mathrm{Na}^{\cdot} \text{ and } n\mathrm{P}'.x\mathrm{NaP}.y\mathrm{H_2O}.$$

Each complex anion or micelle carries n electrons, and the high electrical conductivity is thus reconciled with the high molecular weight.

Flocculation and Peptization. The notion that the charging and discharging of colloid particles is caused by the adsorption of ions is due mainly to Hardy and to Freundlich,[2] but it has been greatly extended by Bancroft,[3] who has used it to interpret certain phenomena which a few years ago appeared extremely puzzling.

It has long been known that the addition of a salt or electrolyte in large quantities to a colloidal solution usually causes precipitation, or "**flocculation.**" Yet, often, the presence of a small quantity of a salt is absolutely necessary for the existence of a colloid solution. Sometimes, for instance, when an insoluble precipitate is shaken up with water containing a small quantity of a salt or electrolyte, the precipitate breaks up, yielding a colloidal solution; the process, as has already been mentioned, is called "**peptization.**" Occasionally, a salt which causes peptization when present in a small quantity will produce flocculation when present in considerable strength.

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[1] J. W. McBain, M. E. Laing, A. F. Titley, M. Taylor, H. M. Bunbury and H. E. Martin, *Trans. Chem. Soc.* **105** (1914), 417, 957; **113** (1918), 435; **115** (1919), 1279, 1300; **117** (1920), 1506.

[2] H. Freundlich, *Zeitsch. Phys. Chem.* **73** (1910), 385.

[3] W. D. Bancroft, *J. Phys. Chem.* **20** (1916), 85; *Trans. Amer. Electrochem. Soc.* **27** (1915), 175, 195; **37** (1920), 55.

Consider first the process of *peptization*. Freshly precipitated ferric hydroxide is peptized by ferric chloride; for some reason, the positive ferric ions ($Fe^{\cdot\cdot\cdot}$) are adsorbed more readily than the chlorine ions. The ferric hydroxide, therefore, acquires a positive charge, and is able to break up into particles, which remain suspended as a stable colloidal solution. It is noteworthy that the hydroxide of any metal generally appears to have a special capacity for adsorbing the ion of that same metal; thus ferric hydroxide is peptized by ferric chloride, aluminium hydroxide by aluminium chloride, and chromium hydroxide by chromium chloride.[1]

The reverse phenomenon of *flocculation* can now be considered. If a negative ion is added to the liquid which is strongly adsorbed by the positive colloid particles, the charge on the particles will thereby be neutralized. The hydroxyl ion, for instance, is strongly adsorbed by ferric hydroxide particles, and consequently if a trace of alkali is added to the positive colloid solution of ferric hydroxide, precipitation at once occurs. This is without doubt due to the neutralization of the positive charge. For if, instead of adding the alkali to the colloidal solution, the colloidal solution is added to the alkali, so that the latter is always in excess, the colloid particles pass quickly through the neutral state and acquire a negative sign before time has been allowed for precipitation to occur; the negative colloid produced is then perfectly stable.

Although chlorine ions are less readily adsorbed than the ferric ions, yet if the chlorine ions are present in considerable excess, sufficient adsorption may occur to cause electrical neutrality and consequent precipitation. Thus, by adding potassium chloride in moderate concentration to the positive ferric hydroxide sol, precipitation occurs. The addition of an equivalent amount of mercuric chloride, which is hardly ionized, has no such effect.

In the precipitation of *positively* charged colloids like ferric hydroxide, it is the adsorption of an *anion* which is the determining factor; on the other hand, for the flocculation of *negative* colloids, the nature of the *cation* is of paramount importance.[1] In both cases, it is found that divalent ions are generally more effective than monovalent, and trivalent ions are generally more effective still. Thus, in the precipitation of a negative colloid such as arsenic sulphide, salts of calcium are more effective than salts of sodium, but salts of aluminium are more effective still. It should, however, be pointed out that in many cases the adsorption of different monovalent, divalent and trivalent ions differ greatly among themselves.[2]

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[1] J. N. Mukherjee, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 103, brings forward the interesting view that "the fixation of a common ion is due to the same causes that bring about the growth of a crystal in its solution."

The dependence of the precipitation of a positive colloid upon the anion, and that of a negative colloid upon the cation, is shown by the following numbers.[3] They indicate, in the case of three different salts, the equivalent concentration needed to cause the precipitation of two typical colloids.

	Concentration needed to precipitate Arsenious Sulphide (Negative Colloid).	Concentration needed to precipitate Ferric Hydroxide (Positive Colloid).
Potassium chloride . .	$49 \cdot 5 \times 10^{-3}$ normal	$9 \cdot 03 \times 10^{-3}$ normal.
Potassium sulphate .	$65 \cdot 6 \times 10^{-3}$,,	$0 \cdot 204 \times 10^{-3}$,,
Barium chloride . .	$0 \cdot 691 \times 10^{-3}$,,	$9 \cdot 64 \times 10^{-3}$,,

It will be noticed that, for the *negative* colloid, arsenious sulphide, where the *cation* is of importance, the same order of equivalent concentration is required with potassium chloride as with potassium sulphate; but that, when barium chloride is used as the precipitant, a far smaller concentration suffices, the cation being in this case divalent.

On the other hand, in the precipitation of ferric hydroxide, a *positive* colloid, the *anion* is of importance; here barium chloride has roughly the same precipitating power as potassium chloride, but potassium sulphate, having a divalent anion, is a far more active precipitant.

It is worth while at this point to call attention to the fact that there are two classes of ions which are especially active in colloidal changes[4]:—

(*a*) *Light, mobile, monovalent* ions like hydrion ($H^{\cdot}$) and hydroxyl (OH'). These are specifically adsorbed by the *uncharged* colloidal substance, and confer their charges upon it; thus they are more active as *peptizing agents* than as flocculating agents.

(*b*) *Polyvalent* ions such as $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, SO_4'', $(Fe(CN)_4)''''$ which are readily adsorbed by *charged* colloid particles of opposite electrification, thus neutralizing the charge. Such ions are more active as *flocculating* agents than as peptizing agents.

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[1] W. B. Hardy, *Zeitsch. Phys. Chem.* **33** (1900), 385.

[2] W. D. Bancroft, *J. Phys. Chem.* **19** (1915), 363; *Trans Amer. Electrochem. Soc.* **37** (1920), 55.

[3] H. Freundlich, *Zeitsch. Phys. Chem.* **73** (1910), 386.

[4] N. Bach, *J. Chim. Phys.* **18** (1920), 61.

It is noteworthy that when a colloid which owes its charge to a monovalent ion is treated with excess of a solution containing a polyvalent ion of opposite sign, the colloid is not merely deprived of its charge, but in some cases a reverse charge is conferred upon it. According to Mukherjee, this reversal of charge is rarely brought about by a monovalent ion.[1]

It will therefore be understood why aluminium salts are so especially efficient in reversing the direction of movement of gold or silver particles, and of the oil-particles in an oil-water emulsion ; in each case, the particles have normally a negative charge, but in the presence of aluminium ions this is converted to a positive charge.

A very interesting phenomenon is the precipitation of one colloid by another. If the colloidal solution of positive ferric hydroxide is mixed with a solution of the negatively charged colloid, arsenious sulphide, in certain proportions, mutual adsorption occurs, and the charge on each kind of particle is neutralized ; consequently both colloids are almost completely precipitated.[2]

On the other hand, the presence in a colloidal solution of a second colloid having the *same* charge sometimes adds materially to the stability of the first. For instance, the pure colloidal solutions of the metals are very unstable, and are precipitated by a trace of almost any salt. But, if a little gelatine or gum is added, the metallic colloid is rendered much more stable ; apparently the particles of the organic "**protective**" colloid coalesce in some way with those of the metal ; the protective colloid can be regarded as a peptizing agent.

It has already been pointed out that the same salt may cause peptization in dilute solution and flocculation when present in greater concentrations. Bancroft gives the following interpretation to this rather remarkable fact.[3] In dilute solution, where there is relatively little adsorption, the most easily adsorbed ion alone attaches itself to the colloid, which thus acquires a charge ; peptization, therefore, occurs. In a more concentrated solution, however, conditions become favourable for the adsorption of the opposite ion also, and neutralization of the electric charge results, with consequent flocculation.

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[1] J. N. Mukherjee, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 106.

[2] Cases of this sort are well discussed by W. D. Bancroft, "Applied Colloid Chemistry," 1921 edition, pp. 225–227 (McGraw-Hill).

[3] W. D. Bancroft, *J. Phys. Chem.* **20** (1916), 102, 103.

It is interesting to note that cases of precipitation by means of electrolytes are known in true suspensions; if some fine clay is shaken up with water, and a salt is added, the clay particles are caused quickly to settle to the bottom. It is found that the salt of a divalent metal such as calcium chloride is much more effective than sodium chloride, whilst a salt of aluminium, a trivalent metal, is an even more powerful precipitant; aluminium sulphate causes the clay particles to settle even when present in quite a low concentration.

The Production of a Colloidal Solution. It is now possible to consider some general methods of producing a colloidal solution. It is right, however, before discussing this subject, to point out that many *emulsoid* colloids, for instance, gum arabic, dissolve in water, or in some other solvent, without any particular trouble. In such cases, it seems probable that the solution produced possesses typical "colloidal" properties simply because the molecules of the dissolved substance are large and will not diffuse readily. There is no need to discuss in detail the method of dissolving such substances, since the method differs but little from those employed to obtain a solution of an ordinary salt like sodium chloride.

But the colloidal solutions which are of particular importance in inorganic chemistry are solutions of substances which, under ordinary circumstances, *are scarcely soluble at all*; these substances can—under certain special conditions—be brought into a state of very fine suspension so as to produce a colloidal solution. In the production of such (*suspensoid*) colloidal solutions, it is clearly necessary to adopt a special procedure and to observe certain precautions—just as in the preparation of a *supersaturated* solution of an ordinary soluble salt like sodium sulphate.

In order to obtain a colloidal solution of a hydroxide, or some normally insoluble salt, there are two courses open. We can either start with the solid insoluble form of the substance, and reduce it to the colloidal condition by suitable treatment, for instance, by the addition of a peptizing agent, or even by mechanical grinding or electric disintegration. We may call this the **method of dispersion.** Alternatively we can start with a soluble salt in the molecular state, e.g. in normal aqueous solution, and, either by the interaction of another solution, or by other means (e.g. hydrolysis), convert it to the insoluble substance required; but the conditions must be so regulated that a precipitate—in the accepted sense of the word—is not produced, and the substance remains suspended as particles of colloidal size; the latter method may be styled the **method of controlled condensation.**

(1) **Method of Dispersion.** If ferric hydroxide is shaken up with a little dilute ferric chloride, a dark red-brown colloidal solution is obtained. The solution is fairly stable in presence of ferric chloride, and a certain amount of the ferric chloride can be removed by dialysis; but if too much is removed, the solution becomes unstable and the precipitate of ferric hydroxide settles to the bottom. As has already been mentioned, the colloidal solution can be regarded as containing a complex basic chloride, but not a basic chloride of any definite composition.

Similarly chromic hydroxide is peptized by sodium hydroxide, yielding a clear green solution. But the chromic hydroxide particles can be separated from the sodium hydroxide by passing the solution through a suitable filter; or, alternately, if the clear solution is allowed to stand for some time, it becomes cloudy owing to the formation of a visible precipitate of chromium hydroxide. After some months practically all the hydroxide present has settled to the bottom as a green precipitate and the liquid above is nearly colourless.[1] This has been interpreted as showing that the green liquid is a colloidal solution, and that a definite soluble "chromite" is not present in any great quantity.

The peptization of aluminium hydroxide by acetic acid is of interest,[2] because here it seems possible to obtain either a colloidal solution or a true salt solution, under different conditions. When freshly precipitated aluminium hydroxide is treated with fairly dilute acetic acid (about 8 per cent.), it appears to pass into solution; but on adding hydrochloric acid to the liquid, a precipitate is at once produced. The liquid appears, therefore, to be a colloidal solution of aluminium hydroxide in acetic acid; it can, of course, be looked upon as a basic acetate, but an acetate of indefinite composition, and containing far less acetic acid than would be needed for the normal aluminium acetate. On examination of the solution in the ultra-microscope, colloid particles may be seen.

On the other hand, if aluminium hydroxide is treated with 40 per cent. acetic acid, normal salt-formation takes place, and the solution apparently consists of ordinary aluminium acetate; under such circumstances, hydrochloric acid yields no precipitate when added to the solution.

Although the precipitated hydroxides of aluminium or iron are most easily peptized by means of a trace of acid or by a soluble salt of the metal in question, yet—if they are washed quite free from the precipitant—the hydroxides are capable of being peptized by pure water. This fact—which is the cause of occasional annoyance in chemical analysis—has been made the basis of a method of preparing the "sols" of ferric and aluminium hydroxides.[1] If for instance a ferric chloride solution is treated with ammonia (excess being avoided), and the precipitated ferric hydroxide is thoroughly washed with water in a centrifuge of special construction, stable sols which are almost free from chlorides are obtained. Presumably the peptizing action of water depends on the preferential adsorption of hydrogen ions over hydroxyl ions, although this fact does not appear to be definitely established.

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[1] C. F. Nagel, *J. Phys. Chem.* **19** (1915), 569; W. D. Bancroft, *Trans. Amer. Electrochem. Soc.* **28** (1915), 351. On the other hand, evidence of the existence of "chromites" has been put forward by J. K. Wood and V. K. Black, *Trans. Chem. Soc.* **109** (1916), 164. The controversy is, of course, largely one of nomenclature.

[2] W. B. Bentley and R. P. Rose, *J. Amer. Chem. Soc.* **35** (1913), 1490. Compare also H. B. Weiser, *J. Phys. Chem.* **24** (1920), 505.

The preparation of colloidal metals by the "arc" method, which is described later, is another example of a dispersion method. It is also possible to obtain colloidal solutions by a process of mechanical grinding.[2]

(2) **Method of Controlled Condensation.** It is well known to the analytical chemist that there are certain conditions which must be avoided if a successful precipitation of a sparingly soluble salt is to be brought about. The presence of certain substances are known to interfere with the formation of a precipitate, or to cause the precipitation in so fine a form that the substance fails to settle and passes through ordinary filter-paper. Such substances include sugar, gelatine, dextrin, rubber, albumin, and many of the constituents of organic tanning-materials.[3] The presence of sugar prevents the precipitation of ferric hydroxide which would normally occur on the addition of ammonia to a ferric salt solution; it likewise prevents the precipitation of silver chromate by the interaction of a soluble silver salt with a soluble chromate, a red liquid being produced which only slowly becomes cloudy. Gelatine interferes with the precipitation of silver iodide by the interaction of silver nitrate and potassium iodide. The reason for the absence of precipitation in the presence of these substances may vary; in some cases, perhaps, it may be due to the increased viscosity of the solution; in other cases, it may be due to the formation of definite complex ions; but, in many cases, it is necessary to regard the added substance as a peptizing agent or a "protective colloid," which combines with the compound whilst it still exists as separate par-

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[1] R. Bradfield, *J. Amer. Chem. Soc.* **44** (1922), 965.

[2] G. Wegelin, *Koll. Zeitsch.* **14** (1914), 65; H. Plauson, *Zeitsch. Angew. Chem.* **34** (1922), 469, 473.

[3] C. A. Lobry de Bruyn, *Ber.* **35** (1902), 3079. See also N. G. Chatterji and N. R. Dhar, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 122.

ticles of colloidal size, and prevents these particles from uniting to form a " precipitate " in the ordinary sense of the word.[1]

In some cases, one of the reacting substances appears to play the part of a peptizing agent. If a solution of arsenious acid is poured drop by drop into a solution of hydrogen sulphide, through which carefully purified hydrogen sulphide gas is allowed to bubble, a yellow colloidal solution of arsenious sulphide is obtained; the particles possess a negative charge.[2] But if an acid or a salt is present in the solution used, a precipitate is obtained instead of the colloidal solution. No doubt, in the absence of a flocculating electrolyte, the (HS)′ or S″ ions of the hydrogen sulphide are adsorbed by the colloidal particles, conferring upon them a negative charge.

Generally speaking, the presence of salts in solution, and the heating of the solution, enables the analyst to avoid the formation of colloid solutions. Nevertheless, cases do arise in analysis where the precipitation is apt to be incomplete, or where the precipitate produced is a sticky semi-soluble one, which penetrates into the pores of the filter-paper, and causes them to become blocked. In such cases, a slight knowledge of colloid chemistry may be of great help to the analytical chemist.

A very interesting case of a different character occurs when silver nitrate and sodium chloride are mixed in dilute solution.[3] If the two salts are present in equivalent proportions no colloidal solution is formed. But, if either constituent is in excess, although the solubility limit of the silver chloride is actually diminished, a colloidal solution (or fine suspension) of silver chloride is obtained. If the sodium chloride has been added in excess, the colloidal particles move, on electrolysis, to the anode, having adsorbed Cl′ ions; on the other hand, if the silver nitrate has been added in excess, they adsorb Ag˙ ions, and move to the cathode.

The production of a " sol " of ferric hydroxide by the hydrolysis of a ferric salt solution, accompanied by dialysis to remove the hydrochloric acid formed, is another example of a method of " controlled condensation." In general, neutral solutions of salts of the heavy metals yield, as the result of hydrolysis, hydroxides in particles of colloidal size; but if the solutions are concentrated and especially if certain flocculating electrolytes are present, the particles often join together to form aggregates and a visible precipitate is produced. The preparation of hydroxide " sols " by hydrolysis and dialysis is usually a slow process, but the dialysis is greatly hastened if conducted at an elevated temperature (75–80° C.).[1]

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[1] Compare S. Odén, *Svensk. Kem. Tidskr.* **5** (1920), 74; abstract, *J. Chem. Soc.* **118** (1920), 600.

[2] H. Freundlich, *Zeitsch. Phys. Chem.* **44** (1903), 129.

[3] A. Lottermoser, *J. Prakt. Chem.* **72** (1905), 39; **73** (1906), 374.

Colloidal Solutions of the Metals.[2] The preparation of the colloidal solutions of the metallic elements requires rather special discussion. It is possible to start with metal in the form of ordinary wire or rod, and to convert it to the colloidal state by Bredig's method of **electrical disintegration.**[3] If two gold wires are connected to a battery or dynamo yielding 30–40 volts, and are brought close together beneath the surface of very pure water, so that an "arc" is struck between them, the liquid acquires a blue or purple-red colour. This is a sign of the disintegration of the gold poles, caused by the heat of the discharge. It probably occurs mainly through volatilization followed by condensation of the vapour in the water, but partly also by the detaching of molten drops of metal from the hot tips of the wire; these drops solidify to form globules, which are considerably larger than the particles formed by the condensation of gaseous metal.[4] When the solution is examined under the ultra-microscope, colloidal particles of gold can be observed. The particles have a negative charge, for they move towards the anode when an E.M.F. is applied to the solution. On adding a salt or acid to the solution, a dark precipitate is generally obtained, which consists of finely divided gold.

If in the place of gold, silver poles are used, a grey or reddish-brown solution of colloidal silver is prepared; by the employment of platinum wire, a dark brown colloidal solution of platinum is obtained. By the use of lead or zinc wire, these metals also can be prepared in the colloidal state, but the preparations very easily suffer oxidation.

In these solutions, the colloidal particles are sometimes negatively charged, sometimes positively charged. Since they can be formed in water practically free from salts, it is likely that they owe their charge to adsorbed hydroxyl ions or hydrogen ions obtained from the water itself. It is noteworthy, however, that in various cases, the presence of a very small amount of alkali (for instance, 0·001 normal concentration) is favourable to their formation, whilst in other cases traces of acid, or even of chlorides in the water, is an advantage in the preparation. But the solutions obtained by the arc method are in all cases extremely unstable; and the addition of electrolytes in quantities exceeding the minute traces just indicated may cause a colour-change in the solution, and if present in still larger amount may throw down a brown or blackish precipitate of the metal in question; the solutions are indeed likely to deposit a precipitate when stored, owing to the accidental access of traces of salts.

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[1] M. Neidle and J. Barab, *J. Amer. Chem. Soc.* **39** (1917), 71.

[2] See R. Zsigmondy, "Chemistry of Colloids"; translation by E. B. Spear (Chapman and Hall).

[3] G. Bredig, *Zeitsch. Angew. Chem.* (1898), 951.

[4] Th. Svedberg, "Formation of Colloids" (Churchill) (1921). Other views are expressed by C. Benedicks, *Koll. Chem. Beihefte*, **4** (1912–13), 229. Compare J. Mukhopâdhyaya, *J. Amer. Chem. Soc.* **37** (1915), 292; H. T. Beans and H. E. Eastlack, *J. Amer. Chem. Soc.* **37** (1915), 2667; V. Kohlschütter, *Zeitsch. Elektrochem.* **25** (1919), 309.

Metallic colloidal solutions are also produced by reduction of the solutions of soluble salts; by treating gold chloride solution containing sodium carbonate with formaldehyde, the chlorine is removed by the formaldehyde and an intense red solution of colloidal gold is obtained. This form of solution can be preserved for some months if precautions are taken to prevent the access of flocculating electrolytes; in preparing it, for example, it is advisable to avoid the use of soft-glass flasks or stirring-rods.[1]

When a little sodium chloride is added to a red solution of gold, the colour is changed to blue; the colour change is due to a partial flocculation, the minute particles of the original red solution uniting together to form larger "secondary aggregates." If the concentration of sodium chloride becomes great, a dark precipitate of finely divided gold is produced. Zsigmondy, who has studied these gold sols in great detail, lays great stress on the distinction between the primary particles, which are present in the red solutions, and the secondary aggregates present in the blue solutions. The former are thought to be massive, whilst the aggregates are loosely assembled and threaded by channels containing the liquid. A similar process of aggregation probably takes place during the flocculation of colloidal solutions of other substances, as well as during the setting of a gel.[2]

Other salts when added to gold sols bring about the same change from red to blue; the union of the gold particles to form larger aggregates is explained by the fact that the salts in question cause partial or total neutralization of the charge on the colloid particles. Strontium chloride, for instance, has been shown first to reduce, then to neutralize, and finally—if added in larger amounts—to reverse the charge of the gold particles; the colour changes from red to blue before the iso-electric point is reached.[3] Where, however, a "protective" organic colloid, such as gelatine or gum, is added, the colloidal solutions of metals often become quite stable, and comparatively large quantities of salts can be added without causing any effect. Certain substances, obtained by the action of sodium hydroxide on egg albumin, known as sodium protalbinate and sodium lysalbinate, have proved of considerable service in the preparation of colloidal solutions of metals; they are usually employed in connection with hydrazine hydrate as a reducing agent. By adding hydrazine hydrate to a solution of a metallic salt containing sodium lysalbinate, stable colloidal solutions of platinum, palladium and iridium have been produced [1]; the solutions can be freed from salts by dialysis, and can be preserved without fear of spontaneous decomposition. In most cases no precipitation is produced even when concentrated sodium chloride is added to the solution. Indeed it is possible to evaporate the solution to dryness, and obtain the protected colloid in a dry form, which readily dissolves again in water, giving the colloid solution.

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[1] C. Thomae, *J. Prakt. Chem.* **80** (1909), 518.

[2] See R. Zsigmondy, "Kolloidchemie" (Spamer). Also R. Zsigmondy, *Zeitsch. Phys. Chem.* **98** (1921), 14.

[3] R. Zsigmondy, *Zeitsch. Elektrochem.* **23** (1917), 151.

In these "protected" colloidal solutions, the metal seems to exist in union with the particles of the organic colloid, and the solution in some ways possesses the properties of the organic colloid rather than of those of the metal in question.

Colloidal solutions of the metals have considerable activity as catalysts. A small amount of colloidal platinum will bring about the decomposition of hydrogen peroxide, and colloidal palladium will aid the combination of hydrogen with unsaturated organic bodies. A certain amount of interest—both practical and theoretical—attaches to the question as to whether the "protected" solution will be a more active or a less active catalyst than the unstable unprotected colloid. The evidence available [2] appears to show that if a protective colloid like gum arabic is added in small amounts to a palladium chloride solution, and if subsequently hydroxylamine is added to reduce the palladium to the metallic condition, the colloidal solution obtained may be a more active catalyst than if the gum arabic were omitted; no doubt the gum acts as a peptizing agent causing the palladium to remain in small particles, which present a large surface area—a condition evidently favourable to catalysis. If, however, an undue amount of gum has been added, the catalytic activity is again reduced; probably the gum tends—under these conditions—to reduce the active palladium surface, by covering it up. It appears, however, that when gum or gelatine is added to a colloidal solution of platinum *after* the reduction to the metallic state, the catalytic activity of the platinum, as determined by the rate of decomposition of hydrogen peroxide, is always reduced.[1]

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[1] C. Paal and C. Amberger, *Ber.* **37** (1904), 124. According to R. A. Gortner, *J. Amer. Chem. Soc.* **42** (1920), 595, the protective value of protalbinates and lysalbinates is greatly inferior to that of ordinary gelatine.

[2] E. K. Rideal, *J. Amer. Chem. Soc.* **42** (1920), 749.

Many other cases are known in which a metal is produced in particles of colloidal size. When solid silver chloride is exposed to light, it undergoes a partial decomposition and acquires a violet colour, which is believed to be due to the presence of colloidal silver particles dispersed through the mass of unchanged salt. The colour varies with the conditions and with the presence of other substances—as is well known to photographers.

When molten metallic lead is added to molten lead chloride, the mass becomes dark owing to the appearance of minute globules of metallic lead; the phenomenon is known as a "**metallic fog.**" When the lead chloride is allowed to cool, the crystals produced are still translucent, but are dark and cloudy owing to the presence of lead particles of colloidal size dispersed through them.[2] The particles can be seen by means of the ultra-microscope.

Another case in which colloidal particles of a metal are dispersed through a rigid substance is that of ruby glass, the colour of which is due to colloid particles of gold (or, in one variety, copper) similar to those present in the red colloidal solutions of gold described above.

Gels. It has been pointed out that the majority of the inorganic substances which—under special conditions—can be obtained as "suspensoid" sols are substances which, under ordinary circumstances, are insoluble and unaffected by water. Many organic "emulsoid" colloids, however, notably gelatine, suffer a great change if brought into contact with water. Solid gelatine, for instance, **swells** when placed in water, forming a jelly or "gel"; on warming, the "gel" liquefies, yielding a "sol," but when the "sol" is again allowed to cool, it once more **sets** to a "gel." The interesting feature of setting is that the whole volume of the "sol" reverts to the gel-form; under ordinary circumstances, no free water is left behind after the setting.

Gels are met with in many metallic compounds; but since nearly the whole of our knowledge of the character of gels is based on the study of organic colloids, it is necessary to take most of our examples here from organic chemistry.

The gel, or jelly, has many of the properties of a solid, although the rigidity varies very much according to the proportion of colloid present, and usually varies somewhat with "age." Very dilute solutions of gelatine do not actually set to a jelly, although they become very viscous when cooled to ordinary temperatures, the viscosity increasing with the time.[1] Even in a concentrated solution the passage from the viscous "sol" to the solid "gel" is a somewhat gradual one. If the change in a gelatine solution be followed by means of viscosity measurements, it is found that the viscosity—which rises slowly for a time—afterwards commences to rise comparatively quickly, and the time at which this quick rise occurs may be regarded as the time of "setting."[2]

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[1] T. Iredale, *Trans. Chem. Soc.* **119** (1921), 109; A. de G. Rocasolano, *Comptes Rend.* **173** (1921), 234.

[2] R. Lorenz and W. Eitel, *Zeitsch. Anorg. Chem.* **91** (1915), 46.

The absorption of water into gelatine during the process of swelling recalls to mind the taking up of water by a sponge. Since, as we have seen in Chapter V, ions can move through a jelly under the influence of an electric current, almost as readily as through liquid water, it would appear that there exist continuous liquid channels, or pores, throughout the whole volume of any jelly. On the other hand, the comparative rigidity of a jelly, and its familiar power of "shimmering"—that is, of performing elastic vibrations—suggests that there is something in the nature of a continuous solid framework.[3] This leads us to postulate a "two-phase" structure, comparable to that of a sponge or honeycomb; according to this view, a solid framework built up of colloid particles in close union is threaded by continuous channels containing a liquid phase.

At the same time, it should be remarked that many physicists adhere to the view that a gel is a homogeneous (one-phase) material. There is no need to enter into this controversy, which is mainly one of definition. It has already been explained that a colloidal solution stands midway between a true solution (a one-phase system) and a coarse suspension (a two-phase system); in just the same way a gel must be regarded as intermediate between a homogeneous (one-phase) glass and a two-phase sponge or honeycomb, the dimensions of the walls and channels being of the same order of magnitude as those of colloidal particles.

As already stated a gel can be obtained (1) by the *setting* of a sol and (2) by the *swelling* of a dry colloid. It is convenient to consider these processes separately.

The Process of Setting. The process of the setting of a sol to a gel has been studied under the ultra-microscope.[4] The results observed are not very easy to interpret, especially since in many cases—notably in gelatine solutions—the typical particles are—in the initial stages of setting—too small to be observed. The observations, however, appear to indicate that the colloid particles unite together during the setting process, and that the process continues as the gel ages. More definite evidence regarding the structure of gels is to be observed in the gels of soap and of fibrin.[1] In such gels it is apparent that the colloidal particles have united together in strings to form fibrils and filaments. Probably the filaments actually observed in the ultra-microscope are only the exceptionally big ones, the typical filaments that make up the jelly being too small for detection. However, the presence of these visible fibrils does seem to indicate the tendency to form a filament structure during the process of " setting."

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[1] C. E. Davis, E. T. Oakes and H. H. Browne, *J. Amer. Chem. Soc.* **43** (1921), 1526. Sometimes the viscosity after reaching a maximum begins to decrease again, but this is due to putrefaction.

[2] Compare A. O. Rankine, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 54.

[3] The elastic properties of gels are studied in detail by S. E. Sheppard, and S. S. Sweet, *J. Amer. Chem. Soc.* **43** (1921), 539.

[4] W. Bachmann, *Zeitsch. Anorg. Chem.* **73** (1911–12), 125. Compare W. Mentz, *Zeitsch. Phys. Chem.* **66** (1909), 129; R. Zsigmondy, *Phys. Zeitsch.* **14** (1913), 1098.

It is probable that the ultimate constituents, i.e. the colloid particles of the gel, are the same as those of the colloidal solution; but, whereas in the colloidal solution they move about independently, and display Brownian movement, in the gel the particles have gathered into threads or networks of comparative stability; it is this network structure which apparently causes the mechanical and elastic properties of the gel. " Brownian movement " appears never to be observed in a soap solution after gelatinization has set in[2]; in a gelatine solution, as setting takes place, the free " translatory " movement (Brownian movement) is gradually replaced by an oscillatory movement about fixed points, and this oscillatory movement diminishes in amplitude as the setting process continues.[3]

Apart from questions of mechanical rigidity and elasticity, the properties of a " gel " and a " sol " are extremely similar. Laing and McBain have compared the properties of a certain soap (sodium oleate) in the " gel " and " sol " forms, and have found them to be identical in conductivity, refractive index, concentration of sodium ions and osmotic activity—a striking proof of the ultimate similarity of a " sol " and a " gel."

On the other hand, they consider that a soap " curd "—such as is obtained on cooling a hot concentrated solution of the soap—is essentially different from a " gel "; a curd is the result of the " crystallizing out " of the soap in the form of long fibres which interlace producing a felted mass; the space between the fibres is filled with the saturated solution, with which they are in equilibrium. The individual fibres may be many centimetres long, but are often of barely microscopic diameter.

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[1] J. O. Wakelin Barratt, *Trans. Faraday Soc.* **16** (1921), Appendix, p. **49**; *Biochem. J.* **14** (1920), 49; W. F. Darke, J. W. McBain and C. S. Salmon, *Proc. Roy. Soc.* **98** [A] (1921), 399.

[2] M. E. Laing and J. W. McBain, *Trans. Chem. Soc.* **117** (1920), 1517.

[3] See W. Bachmann, *Zeitsch. Anorg. Chem.* **73** (1912), 144.

Analogy between Setting and Crystallization. There seems little doubt that gelatinization is governed by many of the same general laws as is crystallization. Gelatinization appears to start from nuclei, for a gelatine solution sets more quickly if solid gelatine is added to it. Indeed a case has been described in which a "gel" after setting was found to have the polygonal structure characteristic of cast metals [1]; it is difficult to avoid the conclusion that, in such a gel, the setting has commenced at definite points within the liquid and spread outwards until the jelly mass advancing from one point has come into contact with that advancing from another, producing the well-known polygonal structure.

It is possible to push the analogy further and to apply von Weimarn's principle to the case of gelatinization. In the last chapter it was explained how, in the precipitation of a sparingly soluble salt, a high degree of supersaturation leads to precipitation commencing at a large number of points, producing a fine precipitate, whilst a low degree of supersaturation leads to a coarse precipitate. So also, in the setting of a concentrated gelatine solution, gelatinization appears to commence at innumerable points close together, but when a dilute gelatine solution (0·4 per cent.) is allowed to evaporate spontaneously at ordinary temperature, gelatinization commences at comparatively few points, and we obtain separate spherical grains large enough to be distinguished under the microscope.[2]

It is, however, illogical—in the opinion of the present writer—to assume that because gelatinization obeys the same qualitative laws as crystallization, it should be regarded as a species of crystallization. It would indeed be very strange if von Weimarn's principle did not extend to all changes which spread from a nucleus outwards; the chance of the spontaneous production of a nucleus at any given point in a solution is increased as the solution becomes more and more supersaturated, and we may expect the number of nuclei produced in 1 c.c. of liquid to increase as the supersaturation is increased. This argument is quite independent of the nature of the change, and will hold good whether we suppose crystallization and gelatinization to be identical phenomena or distinct phenomena.

In the opinion of the present writer, gelatinization is *not* a form of crystallization, but consists in the joining up of the primary colloid particles in interconnected strings so as to form a continuous network. Of course the view that gelatinization is distinct from crystallization in no way excludes the possibility that the *colloid particles themselves* may have a crystalline character, as is undoubtedly, in certain colloids, the case.

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[1] W. B. Hardy, *Proc. Roy. Soc.* **87** [A] (1912), 29.

[2] S. C. Bradford, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 44.

The Process of Swelling. The second method of producing a gel—by placing the dry colloid in a liquid, and allowing it to "**swell**"—has also received careful study.[1] Gelatine swells to a greater volume in acidified water than in water containing a neutral salt; it is also swollen by alkalis. If the swelling powers of different acid, neutral and alkaline solutions are compared, the minimum swelling is found roughly to correspond to the "iso-electric point."[2] Since peptization is also at a minimum at the iso-electric point, it follows that swelling is closely akin to peptization. Swelling agents, like peptizing agents, are those which confer a charge on the colloid—no doubt through the selective adsorption of a positive or negative ion. But whereas in peptization the colloid breaks up and becomes dispersed throughout the solution, in "swelling" the solution employed is absorbed into the interior of the colloid mass, which visibly increases in volume. The factor that appears to decide whether swelling can take place without peptization is presumably the cohesion of the colloid substance. Gel-forming substances—glue, rubber, isinglass, silicic acid—are all substances of high cohesion. Thus in gelatine, which has already become swollen through the absorption of a quantity of water—although the different particles have been to some extent forced apart from one another by the water—they remain linked up as strings or networks of sufficient strength to confer rigidity and elasticity on the jelly. On the application of heat, the thermal agitation causes the strings to break up; the jelly loses its rigidity and a colloidal solution is formed; but the attractive forces between the particles do not vanish completely, being responsible for the high viscosity of the liquid.

In the swelling of rubber by organic liquids (chloroform, benzene, etc.) the swelling may continue until a point is reached at which the cohesion of the gel vanishes and the whole breaks up into a colloidal solution.[1] The volume to which a given mass of rubber will swell before breaking down appears to be roughly independent of the liquid absorbed; presumably the point at which the gel changes into a sol represents the point at which the maximum strength of the distended strings of particles is exceeded, and they break asunder.

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[1] H. R. Procter, *Trans. Chem. Soc.* **105** (1914), 313; *J. Roy. Soc. Arts.* **66** (1918), 747; *Trans. Faraday Soc.* **16** (1921), Appendix, p. 40; H. R. Procter and J. A. Wilson, *Trans. Chem. Soc.* **109** (1916), 307. It lies outside the scope of this book to consider the mechanism of swelling, and the application of the so-called "Donnan equilibrium." Those interested should consult the references just given and also F. G. Donnan and A. B. Harris, *Trans. Chem. Soc.* **99** (1911), 1554. See also J. Loeb, *J. Gen. Physiol.* **4** (1922), 351.

[2] D. J. Lloyd, *Biochem. J.* **14** (1920), 152. See especially Fig. 4. Also J. Loeb, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 153. Compare C. R. Smith, *J. Amer. Chem. Soc.* **43** (1921), 1350, who finds that the osmotic pressure of a gelatine "sol" (and probably that of a gelatine "gel") is a minimum at the iso-electric point.

Gelatinous Precipitates. It has already been suggested that, when an aqueous sol "sets" to a gel, the gelatinization generally starts from nuclei within the liquid, just like the crystallization of a molten metal, and extends outward from these points until the whole of colloid is in the gel-form. If the original concentration of the colloid was high—so that the whole of the water present is included within the gel produced—the jelly growing from one nucleus will meet that growing from another, and so the whole liquid will—at the end—turn to a single coherent mass of jelly.

If, on the other hand, the concentration of colloidal substance is low, there will still be water between the gelatinous masses, when the whole of the colloidal substance has passed into the gel-form. In such a case, the masses of gel formed sink to the bottom as an incoherent gelatinous precipitate, clear liquid remaining above.[2]

The gradual passage from a true jelly to a gelatinous precipitate as the amount of water is increased is shown clearly by the following observations on the production of chromic hydroxide by the treatment of chrome alum solutions of different concentrations with potassium hydroxide in excess.[3]

Ratio Chrome Alum : Water.	Character of Product.
1 : 9	Whole sets to a good jelly.
1 : 18	Jelly with some water at the top.
1 : 50	Jelly with some water at the top.
1 : 100	Soft jelly below, clear water above.
1 : 800	Gelatinous precipitate below ; water above.

Many other highly insoluble hydroxides—and especially those of aluminium and iron—have a gelatinous character, when obtained by precipitation.

As to whether a precipitate or a jelly is formed depends, however, on several other factors besides concentration. If the particles are but little heavier than the medium in which they are dispersed, and if the liquid is viscous, they will tend to remain suspended when gelatinization commences at different points; such conditions favour the formation of jelly. If the particles are heavy and the liquid non-viscous, the growing aggregates tend to sink and we get a precipitate.[1] This is one reason why in inorganic chemistry it is so much more difficult to get true jellies than when we are dealing with organic emulsoid colloids, which are light and form viscous solutions.

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[1] P. Bary, *J. Chim. Phys.* **10** (1912), 445. Compare Wo. Ostwald, *Koll. Zeitsch.* **29** (1921), 100, who finds that the swelling power of liquids varies with the specific inductive capacity.

[2] Compare the observations of S. C. Bradford, *Biochem. J.* **15** (1921), 553.

[3] E. H. Bunce and L. S. Finch, *J. Phys. Chem.* **17** (1913), 776.

Are Gelatinous Hydroxides real Chemical Individuals? When ammonia or sodium hydroxide is added to a solution of a salt of a metal like iron, aluminium or chromium, the gelatinous precipitate produced is usually referred to as a "hydroxide" and is sometimes written $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$. It is, however, obvious—in view of what has been said above—that, even if the essential constituent of the precipitates be bodies of the type $Fe(OH)_3$, the precipitate is certain to contain water in excess of that indicated by the formula $Fe(OH)_3$ (or $Fe_2O_3.3H_2O$, as it may be written). When the precipitate is heated it loses part of the water, the final composition depending upon the temperature employed, and the pressure of aqueous vapour existing in the atmosphere in which it is heated. The composition varies under different conditions between wide limits, nor is there any definite indication that the process of desiccation is arrested when the composition corresponds to the formulæ $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$, or indeed to any other hypothetical hydrate.[2] For this reason, many chemists consider that the so-called "hydroxides" of iron, aluminium and chromium are not chemical individuals at all, but that they are merely, as it were, sponges of the anhydrous oxides Fe_2O_3, Al_2O_3 and Cr_2O_3 containing variable quantities of water in the capillary channels. Whether this point of view is correct or not, it is clear that all conclusions regarding the existence of definite chemical individuals which have been based by chemists from time to time upon the analysis of "gelatinous" preparations must be regarded as utterly wrong. The composition of such precipitates is entirely variable, and if a gelatinous or slimy mass happens to show, upon analysis, a composition agreeing with some definite formula, the agreement must be looked upon as fortuitous. Before any attempt is made to establish the identity of some chemical individual, it must be obtained in a definite crystalline—or, at least, a "sandy"

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[1] Th. Svedberg, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 8.

[2] Compare J. M. van Bemmelen, *Rec. Trav. Chim.* **7** (1888), 37; *Zeitsch. Anorg. Chem.* **20** (1899), 185; **62** (1909), 1; H. B. Weiser, *J. Phys. Chem.* **24** (1920), 277, 505.

—form. Thus, aluminium hydroxide, when obtained by the slow action of air containing carbon dioxide upon sodium aluminate, is obtained as a sandy precipitate—possibly of a crystalline character—which has a composition accurately corresponding to the formula $Al_2O_3.3H_2O$ or $Al(OH)_3$; but the hydroxide obtained quickly by the action of ammonia on an aluminium salt solution is of a gelatinous character, owing to the high degree of supersaturation involved at the moment of mixing, and the composition is hopelessly variable.[1] It is noteworthy, that, by the treatment of the gelatinous form with dilute sodium hydroxide for some months, it can be converted to a fine crystalline form, consisting of microscopic bar-shaped crystals; and this crystalline form has now a definite composition, $Al_2O_3.3H_2O$.

It appears to the present writer that, if the compact, sandy and crystalline particles obtained by slow processes are hydrated, it is very improbable that the ultimate particles of the gelatinous form obtained by quick precipitation are anhydrous. It is clear that chemical analysis is powerless to show whether a hydrate exists in a gelatinous precipitate, or not; but it does not follow that some physical method may not succeed where the chemical method has failed. The fact that the vapour pressure of these gels varies continuously with the water-content, showing no sudden change at the composition corresponding to a given hydrate, is no argument against the existence of such a hydrate; the vapour pressure of water contained in a narrow capillary tube is well known to be lower than that of water in a wide tube, and, if one imagines that pores of all diameters varying between wide limits exist in the gel, we may expect that the vapour tension will fall off continuously as the water is expelled from the gel, whether any definite hydrate be present or not.

There are, as a matter of fact, two separate reasons why substances in a fine state of division will show, on analysis, a departure from the composition of the same substance in a compact state. Both are connected with the fact that the ratio of surface to volume is greater in the case of the dispersed substance than in the compact substance; in other words, the effect of the "surface layer" of atoms—which can be neglected in the case of a compact body—cannot be disregarded in a finely divided body. The first cause of disturbance, which is important in the case of the gelatinous hydroxides, is the effect of absorbed water clinging to the surface of the particles, or of capillary water contained in the pores. A second cause of possible disturbance, which has scarcely been investigated experimentally up to the present time, may be predicted as a result of our knowledge of the crystal-structure obtained by means of the X-ray method. Consider the crystal-structure of iron pyrites, FeS_2. This is known to be made up of a large number of minute unit cubes, each containing one sulphur atom in the interior, and four iron atoms at certain corners (Fig. 72). The composition of a single cube is Fe_4S, but if a very large number of cubes are placed together, so that the same iron atom serves for the corner of eight cubes, the iron content of the aggregate is reduced to one-eighth, and the formula, instead of being Fe_4S, becomes FeS_2. In arriving at the formula FeS_2, we have, however, neglected to take account of the effect of the surface layers, where a single iron atom cannot serve eight cubes; therefore if the crystals are not moderately large, we may expect a deviation from the limiting composition FeS_2. Iron pyrites particles consisting of 50^3 unit cubes—which should be visible under the ultra-microscope—will have the composition $FeS_{1 \cdot 88}$.[1]

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[1] F. Goudriaan, *Proc. Amst. Acad.* **23** (1920), 129.

There are, therefore, two reasons why finely divided substances may deviate from their "proper" composition, but this does not mean that the particles of a finely divided substance may not be thought of as being built up on a plan which, if continued indefinitely—as is the case in the same substance when in the compact state—would lead to a simple atomic formula. Before we can determine whether "hydroxides" of the type $Fe(OH)_3$ do exist in the slimy precipitates referred to above, we must discover some method which will enable us to distinguish the "combined" water existing in the interior of the component particles of the precipitate from the "capillary water" contained in the pores of the gel, and from the "free" water clinging loosely to the precipitated mass. To distinguish the "combined," "capillary" and "free" water is not easy. A method has been worked out[2] which depends on the expansion observed when the gel is frozen; from this expansion the content of free and capillary water can be calculated and the "combined" water is found by difference. Unfortunately, there is really no good independent method of checking the results, which

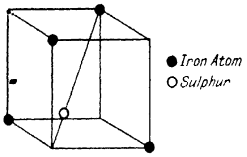

FIG. 72.—Crystal Structure of Iron Pyrites.

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[1] A. Quarteroli, *Gazetta*, **50** (1920), ii. 60. The criticism raised by A. Perucca, *Gazetta*, **51** (1921), i. 255, is answered by A. Quarteroli, *Gazetta*, **51** (1921), ii. 211.

[2] H. W. Foote and B. Saxton, *J. Amer. Chem. Soc.* **38** (1916), 588; **39** (1917), 1103.

must therefore be accepted for the moment with a certain amount of caution.

The amount of capillary and free water naturally varies with the method employed in preparing the gel, and the proportion of combined water obtained by the method is far from constant, and seems to depend upon the age of the gel. One research upon aluminium hydroxide prepared eight months previously by the interaction of ammonia and aluminium chloride showed the preparation to contain 37·1 per cent. of combined water; for the formula $Al(OH)_3$, only 34·6 per cent. is required. It is possible to ascribe the difference of 2·5 per cent. to water held in solid solution. A freshly precipitated sample contained 37·7 per cent. of combined water.

The amount of combined water contained in ferric hydroxide varies within much wider limits according to the method of preparation; it is quite possible that the compound $Fe(OH)_3$ does not exist to any large extent in the precipitate, which may consist mainly of a solid solution of water in Fe_2O_3.

The Question of Basic Salts. Often a precipitate of a "hydroxide" thrown down, say, from a chloride solution includes a quantity of the chloride of the same metal, which is difficult to remove by washing; similarly, a precipitate thrown down from a sulphate solution is often difficult to wash free from sulphate. The salt may be held by surface adsorption, or in solid solution in the hydroxide. Such precipitates have often, in the past, been styled "basic chlorides," or "basic sulphates." They can, of course, be regarded as insoluble basic salts of variable composition, just as the colloidal solution of ferric hydroxide peptized by ferric chloride can be regarded as a soluble basic salt of variable composition. But some chemists have gone farther, and have assigned definite formulæ to them. This is, in most cases, wrong. It is true that many true basic salts such as $PbCl_2.3PbO$ are known which are definite chemical individuals of constant composition. Some of these, for instance $SbOCl$, can be obtained in well-developed crystals and their individual existence is as well established as that of any normal salt. But it is entirely wrong to assume—as has often been done in the past—that, because chlorine—or some other acid radicle—is found in a gelatinous precipitate after continued washing, a new basic salt has been prepared. The precipitate may be an adsorption product, or a solid solution of a salt in a hydroxide. Even if a basic salt is present, it may not have a formula corresponding to the composition of the precipitate, which may consist of a mixture of two or more basic salts. Before the existence of a basic salt as a definite chemical individual can be admitted, the composition must be shown to remain constant even when the composition of the solutions used for the precipitation are varied to a very considerable extent.[1]

As an example of the tenacity with which adsorbed ions are held by a precipitate may be mentioned the case of arsenious sulphide. When a colloidal solution of arsenious sulphide (a negative colloid) is precipitated by the addition of barium chloride, it is the barium ions which actually cause precipitation, and it is found impossible afterwards to wash the precipitate free from adsorbed barium.[2]

Physical Character of the Colloid Particles. Graham, who is often regarded as the originator of colloid chemistry, considered the colloidal state as the antithesis of the crystalline state. It appears, however, almost certain that in many cases the colloid particles have actually a crystalline character. X-ray work on colloidal solutions of gold and silver, for instance, appears to show without doubt that the metallic particles are minute crystals.[3] The optical properties of colloidal solutions of vanadium pentoxide appear to point to the existence of particles having some at least of the properties of crystals.[4] Furthermore, if von Weiman's view—referred to in the last chapter—is accepted, and we agree that apparently amorphous gelatinous precipitates are really crystalline in character, it is difficult to avoid the view that the ultimate particles of jellies, also, are really crystalline particles.

In assuming a crystalline character for the ultimate colloid particles of sols and gels it is not intended to suggest that the outline of the particles corresponds in every case to a perfect geometrical form; in many cases they are probably best regarded as roughly spherical; the word "crystalline" is used only to describe the internal arrangement of the atoms. Von Weimarn's work on barium sulphate may be recalled once more. From very dilute solutions, this salt is precipitated in geometrical forms, from rather more concentrated solutions in dendrites, from solutions of average concentration in the familiar fine "apparently amorphous" form, and from very concentrated solutions in a gelatinous condition. In the latter case, the ultimate particles, which adhere together in flocks, cannot be made out, but it is very unlikely that they possess any definite geometrical form.

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[1] See F. B. Allan, *Amer. Chem. J.* **25** (1901), 307, who treats the question from the standpoint of the "Phase Rule." Also W. L. Miller and F. B. Kendrick, *J. Phys. Chem.* **7** (1903), 259; H. B. Weiser, *J. Phys. Chem.* **24** (1920), 505.

[2] S. E. Linder and H. Picton, *Trans. Chem. Soc.* **67** (1895), 63.

[3] P. Scherrer, *Nachr. Ges. Wiss. Göttingen* (1918), 16; abstract, *J. Chem. Soc.* **116** (1919), 274.

[4] W. Reinders, *Proc. Amst. Acad.* **19** (1916), 189. See, however, the interesting views on this subject put forward by H. Zocher, *Zeitsch. Phys. Chem.* **98** (1921), 293.

Summary. Colloids may be divided into suspensoids and emulsoids; a colloidal solution of a suspensoid character is intermediate between a true solution and a suspension, whilst a solution of an emulsoid is regarded by many chemists as the normal solution of a substance which has naturally large molecules. Colloid particles are small enough to exhibit thermal (Brownian) movement, and yet large enough to be visible—in many cases—in the ultramicroscope. The particles are positively or negatively charged, and move towards cathode or anode when the solution is electrolysed. The charge is essential to stability; if, by addition of an electrolyte, the particles are rendered electrically neutral, flocculation occurs.

The charge is due to the preferential adsorption of certain ions by the particles; the discharge is caused by the adsorption of ions of the opposite sign. The flocculation of negatively charged colloids depends on the nature of the cation of the flocculating electrolyte; the flocculation of positively charged colloids depends on the anion of the flocculating electrolyte. In general, trivalent ions are more effective flocculators than divalent, and divalent more effective than monovalent. Aluminium salts are powerful flocculators of negative colloids. The addition of an aluminium salt to a colloidal solution of gold, or a suspension of oil-drops in water, first neutralizes the negative charge, and then, if added in sufficient quantity, renders the particles or drops positively charged.

When precipitated hydroxides are shaken with dilute salt solutions, or dilute acids or alkalis, they often adsorb ions, and break up into charged colloid particles which remain suspended. This process is known as peptization. Thus ferric hydroxide is peptized by ferric chloride, through the adsorption of ferric ions. The colloid particles can be regarded as the positive ions of the complex salt $[xFe(OH)_3.yFe]Cl_{3y}$, but it is not a complex salt of definite composition.

An alternative method of preparing colloidal solutions of normally insoluble substances is by double decomposition carried out under such conditions that the particles produced, being charged through the adsorption of ions, do not unite together to form a visible precipitate.

Colloidal solutions of the metals can be produced by allowing an arc to pass below the surface of water between electrodes made of the metal in question. They can also be prepared by the reduction of salts. The "sols" are normally unstable, as the particles readily join together to form secondary aggregates; but they are rendered stable by the presence of certain "protective" organic colloids. "Fogged" lead chloride, silver chloride rendered violet by the action of light, and ruby glass all owe their colour to colloid metallic particles.

Gels can be produced by the "setting" of a colloidal solution, or by the "swelling" of a dry colloid. They appear to consist of a solid network, probably formed of strings of colloid particles in union, threaded by continuous liquid channels. The network affords rigidity and elasticity, whilst the continuous channels allow free diffusion. The Brownian movement of the particles vanishes when they unite in chains to form a gel.

Where the proportion of colloid present is insufficient for the gelatinization of the whole liquid, a gelatinous precipitate may be produced, which gradually sinks, leaving a clear liquid above. Such precipitates are found amongst the so-called "hydroxides" of metals like aluminium and chromium; gelatinous precipitates always contain water in variable amount, and it is impossible to assign a definite composition to them as the result of chemical analysis; possibly physical methods may show whether it is correct to regard these substances as being definite hydroxides.

The gelatinous "hydroxides" often also contain considerable quantities of adsorbed salts (chlorides, sulphates, etc.) which are unremovable by washing; such precipitates are often referred to as basic salts, but they should be distinguished from the "basic salts" of definite composition.

Many of the primary particles found in sols and gels appear to have a crystalline character, but this does not necessarily imply a definite geometrical form. The fact that the process of gelatinization follows many of the same laws as crystallization does not imply that the processes are identical.

12 OCT 1925

CHAPTER VIII

DECOMPOSITION VOLTAGE AND THE E.M.F. OF A CELL

Decomposition Voltage of an Electrolytic Cell. It is necessary to return to the phenomena accompanying the passage of electricity through a solution of an electrolyte, as exhibited in an electrolytic cell. It was pointed out, at the commencement of Chapter V, that whereas a metallic conductor is unchanged by the passage of electricity through it, except for a small rise of temperature—the application of a P.D. to a solution may produce both (1) motion and (2) decomposition in the latter.

If we go on to investigate the relation between the Potential Difference which produces the current, and the strength of the current that is produced, an even more striking contrast is obtained between the two classes of conductors.[1] In the case of a metallic conductor, the current produced is—in accordance with Ohm's Law—proportional to the P.D. which gives rise to it; the curve connecting the volts and the amperes will thus be a straight line, as is shown by curve A of Fig. 73, which refers to the current sent through a nickel-chromium wire. On the other hand, if we measure the current forced through an electrolytic cell by an E.M.F. of varying intensity, we obtain a very different result. Curve B indicates the current forced through a zinc bromide solution, carbon electrodes being used. Until the P.D. applied to the system reaches a certain critical value, practically no current is forced through the cell; when once this critical value is passed, the current rises rapidly with any further increase in the applied E.M.F. The critical value is called the Decomposition Voltage. It is true that a momentary current may sometimes be sent through the cell by an E.M.F. of a magnitude less than the decomposition voltage, but this soon falls off as the products of decomposition begin to accumulate at the electrodes, and sinks to an almost negligible quantity. The value of the critical E.M.F. depends on the nature of the solution and the material of the electrodes; it is independent of the shape of the electrolytic cell or the distance between the electrodes.

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[1] See a most instructive paper by O. P. Watts, *Trans. Amer. Electrochem. Soc.* **19** (1911), 91, from which many of the examples are taken.

The cause of the existence of the critical E.M.F. must be found in the decomposition which necessarily accompanies the passage of electricity through the solution. If the electrolytic cell consists of two copper electrodes immersed in copper sulphate solution, the critical E.M.F. is practically nil. Here the effect of the current is to dissolve copper at the anode and to deposit an equal amount at the cathode; the net result is merely a transference of metal from one place to another; since, therefore, there is no chemical work to accomplish, the smallest P.D. will suffice to force current through the cell as is shown in curve C (Fig. 73). But, in the ordinary electrolytic cell, decomposition is brought about; that is to say, the current is called upon to perform chemical work. If the electrolytic cell consists of two carbon electrodes immersed in zinc bromide solution, each 2 × 96,580 coulombs of electricity which passes involves the decomposition of one gram-molecular weight of zinc bromide according to the equation

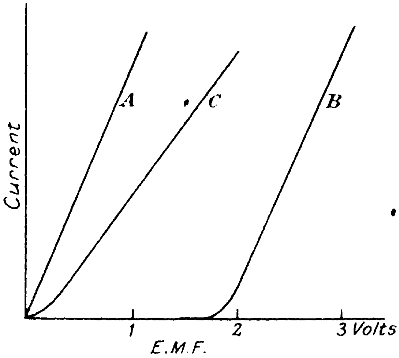

FIG. 73.—Variation of Current with P.D. applied to (A) Nickel Chromium Wire; (B) Zinc Bromide Solution between Carbon Electrodes; (C) Copper Sulphate Solution between Copper Electrodes.

$$ZnBr_2 = Zn + Br_2.$$

Now, when zinc and bromine combine to form zinc bromide in the presence of water, forming a solution of zinc bromide, there is great evolution of heat, amounting to 90,960 calories for the gram-molecular weight.[1] If the zinc bromide is once more to be split into its elements, this amount of energy has to be supplied. Let us assume, for the moment, that it is all to be supplied as electrical energy—and that there is no absorption or evolution of heat in the electrolytic cell. The electrical energy involved when 2 × 96,580 coulombs are forced through the cell by a P.D. of E volts is

$$2 \times 96{,}580 \times \mathrm{E} \text{ joules,}$$

which is equivalent to

$$2 \times 96{,}580 \times \mathrm{E} \times 0{\cdot}24 \text{ calories of heat energy.}$$

If, therefore, this is to be equal to 90,960 calories, E must be equal to

$$\frac{90{,}960}{2 \times 96{,}580 \times 0{\cdot}24} \text{ volts,}$$

that is, to about 1·96 volts.

Actually it is found that the decomposition voltage, below which zinc bromide cannot be decomposed, is 1·80 volts.[2] The discrepancy, amounting to 0·16 volts, is mainly due to the fact that the assumption made above—namely that there is no evolution or absorption of heat in the electrolytic process—is not justified; although, in the electrolytic process, the energy is mainly supplied by means of the electric current, actually a small absorption of heat energy occurs at the electrodes, and consequently a slightly smaller E.M.F. than 1·96 volts suffices to carry out the decomposition.

A similar heat-effect occurs in most cases of electrolysis, although in some cases it is an evolution of heat—instead of an absorption—which is observed at the electrodes. For very rough purposes, however, the heat effect accompanying electrolysis can be neglected, and—if this is done—we can use the argument just employed to obtain a general equation connecting the decomposition voltage, E, and the amount of heat-energy, q, which would be needed to bring about the decomposition of one gram-molecule thermally. The electrical energy which is exerted when a gram-molecule is decomposed at the E.M.F. E is

$$\mathrm{E} \times 96{,}580 \times n \text{ joules,}$$

where n is the number of electrons taken up when one molecule is decomposed (e.g. two for $NiCl_2$; one for $AgNO_3$, etc.; three for $AlCl_3$; and six for $Al_2(SO_4)_3$).

This quantity of energy is equivalent to

$$\mathrm{E} \times 96{,}580 \times n \times 0{\cdot}24 \text{ calories,}$$

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[1] According to J. Thomsen, "Thermochemistry," translation by K. A. Burke (Longmans, Green).

[2] M. Le Blanc, *Zeitsch. Phys. Chem.* 8 (1891), 322.

Discharge . . $Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$

Charge . . $2PbSO_4 + 2H_2O = Pb + PbO_2 + 2H_2SO_4$

In the charged state the negative plates of an accumulator consist essentially of spongy metallic lead supported in a grid or ribbed plate of lead, whilst the positive plates consist of lead peroxide (PbO_2) similarly supported. During the discharge a certain amount of lead sulphate is formed on each plate; the reaction occurring at each plate can be written separately, thus:—

At the negative plate, $Pb + SO_4'' = PbSO_4 + 2e$

At the positive plate, $PbO_2 + 4H^{\cdot} + SO_4'' + 2e = PbSO_4 + 2H_2O$

The reverse changes occur at each plate during the charging.

The critical E.M.F. which should be derived from the heat-evolution (87,200 calories) connected with the change,

$$Pb+PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O,$$

can be calculated roughly from the simple equation

$$E = \frac{q}{n} \times \cdot 000043 \text{ volts.}$$

It should be $\frac{87,200}{2} \times \cdot 000043 = 1 \cdot 87$ volts.

The discrepancy between this value and the 2 volts met with in practice shows that here also—besides the transformation of electrical to chemical energy and vice versa—other transformations of energy must be occurring. As a matter of fact, when a lead accumulator is charged, a certain amount of the electrical energy used up appears as heat which is evolved at the electrodes; during the discharge, an equivalent absorption of heat appears and the accumulator tends to become cooler. This reversible heat-effect at the electrodes accounts for the working E.M.F. being actually about 2 volts, as opposed to the calculated value of 1·87 volts.

Primary Cells. From the accumulator, which acts alternately as an electrolytic (current-absorbing) cell and as an electric (current-producing) cell, it is natural to pass to the primary electric cells, which are designed essentially as producers of current. Consider the Daniell cell; here, the positive pole consists of a copper sheet immersed in a solution of copper sulphate, whilst the negative pole is a zinc stick immersed in zinc sulphate; the two solutions are separated by a porous wall, which prevents undue mixing. When the cell is producing current, metallic zinc enters the solution

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Joubert, *Trans. Amer. Electrochem. Soc.* **37** (1920), 641. The matter is further discussed in Vol. IV in the section dealing with lead.

producing zinc ions, and leaving the zinc rod with an excess of electrons; meanwhile, at the copper sheet, copper ions from the solution take up electrons and form atoms, which appear as a fresh deposit of metallic copper; this process causes a continual production of electrons at the zinc rod, and an absorption of electrons at the copper plate, and so maintains the current. The changes can be expressed thus:—

At the negative pole . . . $Zn = Zn^{\cdot\cdot} + 2e$

At the positive pole . . . $Cu^{\cdot\cdot} + 2e = Cu$

By adding the two changes together, we obtain for the reaction in the cell as a whole,

$$Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu,$$

or, in non-ionic language,

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

If some metallic zinc be introduced into copper sulphate solution, in an ordinary glass vessel, copper is precipitated in a spongy form; the same change

$$Zn + CuSO_4 = ZnSO_4 + Cu$$

is here proceeding, but, since no electric current is produced outside the vessel, the energy is liberated—finally, at least—in the form of heat. By observing the rise of temperature it can be found that 50,110 calories accompany the change. Assuming that, in the Daniell cell, the whole of the energy is liberated in the electrical form, we might expect an E.M.F. of

$$E = \frac{50{,}110}{2} \times {\cdot}000043 = 1{\cdot}08 \text{ volts}.$$

Now this is very close to the actual E.M.F. (1·096 volts) produced by a Daniell cell, and it follows that in this case the chemical energy is transformed into electrical energy without appreciable absorption or evolution of heat at the electrodes. It is not intended to imply that no heat is evolved when a Daniell cell produces current, because the friction of the ions moving through the solutions necessarily causes a slight rise of temperature in the body of the solution. What is practically absent in the Daniell cell is the *reversible* heat-effect *at the electrodes*—the effect which, in the lead accumulator, represents an evolution of heat during charge and an absorption of heat during discharge; we have independent evidence that in the Daniell cell the reversible heat-effect is extremely small.

When it is stated that the E.M.F. of a Daniell cell is 1·096 volts, we really mean that a Daniell cell will "balance" a P.D. of 1·096 volts; if a Daniell cell is opposed to another cell—or source of P.D.

—yielding 1·096 volts, no current will be produced. If, however, the external P.D. be slightly reduced—say, to 1·05 volts—the Daniell cell will commence to furnish current, whilst if the external P.D. is slightly increased—say, to 1·2 volts—current will be forced through the Daniell cell in the opposite direction; in that case, the reverse change

$$Cu + ZnSO_4 = Zn + CuSO_4$$

will presumably occur in the cell, which is for the moment acting as a current-absorber. Although the Daniell cell would scarcely make a serviceable accumulator for practical use, it is possible to regard it as an example of a **reversible cell.**

Most cells of the "Daniell type"—that is, cells consisting of two metals, each immersed in a solution of one of its own salts—are reversible in this sense; a very slight excess of P.D. over the critical value will cause current to flow one way through the cell, whilst a slight deficit will cause it to flow the other way. On the other hand, many cells are not reversible. The simple cell formed when copper and zinc plates are immersed in a dilute acid, for instance, is not reversible. When the cell furnishes current the zinc dissolves, forcing out hydrogen gas on the copper plate. The equation, expressed in ionic language, is

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2.$$

But we attempt to force current through the cell in a contrary direction by means of an external E.M.F., then the copper will have to be forced into solution, the change being probably

$$Cu + 2H^{\cdot} = Cu^{\cdot\cdot} + H_2.$$

The reverse external E.M.F. which must be applied to the cell to produce this result will very much exceed that which is generated when the cell is in action in the normal manner.

The Potentiometer. In order to measure the E.M.F. of a reversible cell, a source of variable P.D. is required, which can be adjusted until it just balances the P.D. furnished by the cell. Such an arrangement constitutes a potentiometer, a convenient form being shown diagrammatically in Fig. 75. A series of electric cells, B, yielding a P.D. (say 4 volts) greater than that of any cell that is likely to come up for measurement, sends a current along the long, thin, uniform resistance wire QR. The wire must have a resistance high compared to all the other conductors of the circuit, and the greater part of the 4 volts provided by the cells should fall over the wire. A sliding-contact P is arranged to move over the wire, and by bringing it to a suitable position, any desired P.D. between Q and P can be obtained at will. When, for instance, P is half-way between Q and R, about 2 volts will be obtained; if P is three-quarters of the distance from Q to R, 3 volts will be obtained; the exact values can be read off on the high resistance voltmeter V.

The cell to be tested is placed at X, one pole being in connection with Q, and the other being joined—through the sensitive galvanometer A, and tapping-key K to the sliding-contact P, the connections being chosen so that the cell opposes the P.D. furnished by the potentiometer. In that case, if the P.D. furnished by the potentiometer is greater than that of the cell, the galvanometer will show current passing in one direction. If the P.D. furnished is less than that of the cell, the galvanometer will register current in the other direction. Only when the P.D. between Q and P is exactly equal to that of the cell, is a "balance" obtained, and no deflection is obtained when the tapping-key is pressed down. The P.D. corresponding to this state of equilibrium is then obtained by reading the voltmeter, V.[1]

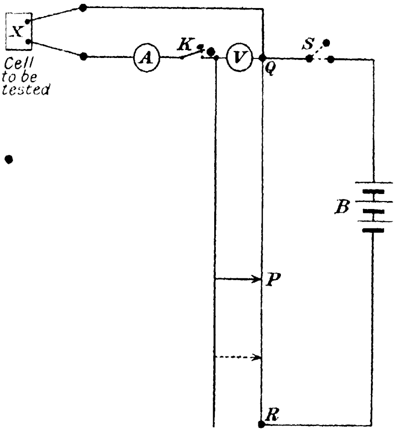

FIG. 75.—The Potentiometer.

If the cell is truly reversible, equilibrium is always obtained at the same point, no matter from which side it is approached. Since at the point of balance there is no current passing through the cell which is being tested, the value is truly the "equilibrium E.M.F." of the cell; no error is caused by the small current which leaks through the voltmeter, because this current is provided by the main battery B, and not by the cell X under examination.

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[1] Many workers prefer to employ a capillary electrometer to a galvanometer for detecting the want of balance between the P.D.s. If properly used the capillary electrometer gives excellent results and is for some classes of work preferable. See H. J. S. Sand, *Trans. Faraday Soc.* **5** (1909), 159. But for ordinary potentiometer work, a galvanometer detector built into the potentiometer box as part of the instrument, is more convenient.

In this respect, the potentiometer method of testing a cell is far more accurate than the rough method commonly adopted of simply joining the cell to an ordinary voltmeter and noting the deflection. In that admittedly more simple method, the current sent through the voltmeter is provided by the cell which is being tested, and the voltage observed is not the "equilibrium E.M.F.," but the E.M.F. of the cell measured whilst producing a current; often it may be very perceptibly less than the equilibrium value. Moreover, as has already been pointed out in the introduction, unless the cell has a resistance very small compared to that of the voltmeter, an important fraction of the total P.D. will fall over the liquid within the cell, and—for this reason, also—the value obtained on the voltmeter will be too low. The potentiometer method is free from both these defects.

Standard Cells. In calibrating or testing a potentiometer, it is of great service to possess a cell—or cells—the E.M.F. produced by which is known with great accuracy. The usual standard employed is the **cadmium cell,**[1] which gives an E.M.F. of 1·0183 volts at 20° C.; the E.M.F. is almost independent of the temperature. The composition of this cell is:—

Cadmium Mercury Amalgam containing 12½ per cent. Cadmium	Saturated solution of Cadmium sulphate containing crystals of $3CdSO_4.8H_2O$	Paste of Hg_2SO_4 and $3CdSO_4.8H_2O$ in water	Mercury

The amalgam electrode forms the negative pole, the reaction there being

$$Cd = Cd^{\cdot\cdot} + 2e,$$

whilst at the mercury pole fresh metallic mercury is deposited from the mercurous sulphate in solution according to the reaction

$$2Hg^{\cdot} + 2e = 2Hg.$$

In the commonest form of the cell, an H-shaped vessel is employed;

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[1] A criticism of the employment of this type of cell as a standard has lately been published by E. Cohen and A. L. Th. Moesveld, *Zeitsch. Phys. Chem.* **95** (1920), 285. See, however, reply by W. Jaeger and H. von Steinwehr, *Zeitsch. Phys. Chem.* **97** (1921), 319.

the mercury and the amalgam occupy the bottoms of opposite limbs, as shown in Fig. 76.[1]

Another standard of potential is the Clark Cell, which consists of the combination

$$\text{Zinc}\;\Big|\;\begin{matrix}\text{Saturated}\\ \text{ZnSO}_4\text{ solution}\end{matrix}\;\Big|\;\begin{matrix}\text{Paste of}\\ \text{Hg}_2\text{SO}_4\end{matrix}\;\Big|\;\text{Mercury}$$

The E.M.F. is 1·434 volts, but it varies with temperature more than the cadmium cell; the variation, however, can be allowed for.

For rough work, the Daniell cell (1·096 volts) can be used as a standard of potential, but it is by no means so constant as the two cells just mentioned.

Many investigators—when using a potentiometer—omit the voltmeter from the arrangement shown in Fig. 75, and calculate the E.M.F. of an unknown cell from the position of the sliding contact at the point of balance. In this method, the stretched wire of the potentiometer must be absolutely uniform so that the potential drop is uniformly distributed over it. A cadmium cell is first attached to the potentiometer at X, and the distance QP measured when equilibrium is obtained; let this be equal to l_1. The cell to be tested is then attached in place of the cadmium cell, and the new position of balance is found; let the new length of QP

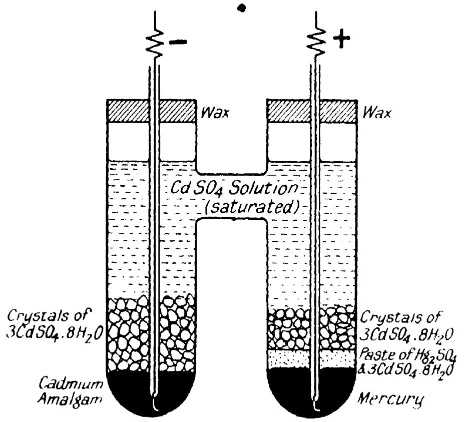

FIG. 76.—Cadmium Cell.

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[1] Another, more compact, form of the cell is described by C. J. Rodman and T. Spooner, *Trans. Amer. Electrochem. Soc.* **38** (1920), 97.

be l_2. Assuming the wire is uniform, the E.M.F. of the cell which is being tested will be $\frac{l_2}{l_1} \times 1{\cdot}0183$ volts.

Summary. Practically no current is forced through an electrolytic cell, and no decomposition is produced, unless the E.M.F. applied to it exceeds a certain critical value (the "decomposition voltage"); this value can be calculated roughly from the heat-absorption which takes place when the same decomposition is brought about thermally. The accumulation of decomposition products at the electrodes causes a "back E.M.F. of polarization"; and unless the E.M.F. applied to the cell exceeds the value of this back E.M.F., clearly no current can pass.

In a primary cell, also, the value of the maximum E.M.F. of the cell is closely connected with the heat evolved when the same reaction occurs without the production of an external current. The maximum P.D. provided by a reversible cell should properly be measured by the method of balance on a potentiometer; direct measurement on a voltmeter—especially a low-resistance voltmeter—yields a value which is unduly low. Cells of the Daniell type are "reversible"; if opposed by another P.D. slightly smaller than the equilibrium E.M.F. of the cell, current flows in one direction, whilst if opposed by a P.D. slightly larger than the equilibrium value, current flows in the opposite direction.

CHAPTER IX

SINGLE ELECTRODE POTENTIALS

The study of the equilibrium E.M.F.s of various cells of the Daniell type—consisting of two metals immersed in solutions of their respective salts—has led to certain most important results. It has been found possible to regard the E.M.F. of the complete cell, as being the difference between two "single potentials" provided by two "half-cells."[1] A few examples will make this clear. The ordinary Daniell cell combination can be expressed thus,

$$Zn \mid ZnSO_4 \vdots CuSO_4 \mid Cu$$

or, in ionic language,

$$Zn \mid Zn^{\cdot\cdot} \quad \mid Cu^{\cdot\cdot} \quad \mid Cu$$

Since the E.M.F. produced by the cell is independent of its shape and the distance between the electrodes, but varies with the composition of the electrodes and the concentration of the solutions, it is natural to attribute it to the interfaces between the metals and the solution. It has become customary to regard the two interfaces

$$Zn \mid \begin{matrix} ZnSO_4 \\ \text{solution} \end{matrix}$$

and

$$\begin{matrix} CuSO_4 \\ \text{solution} \end{matrix} \mid Cu$$

as each producing a characteristic P.D.; the combination of the two gives the resultant E.M.F. of the complete cell. Necessarily, the E.M.F. provided by the complete cell will be the *difference* between the single potentials of the two half-cells, not the *sum*; for, if the two half-cells are identical, as in the cell

$$Cu \mid CuSO_4 \mid CuSO_4 \mid Cu$$

the E.M.F. of the combination will be zero.

Such a conception can only be of value if it is known that a given half-cell keeps its characteristic P.D. unchanged in all combinations, irrespective of the nature of the other half-cell with which it is combined. Before proceeding farther, we must test this point. The E.M.F.s of the following three cells have been measured :—[1]

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[1] Strictly speaking, the E.M.F. of the complete cell is the *difference between the differences of potential* existing at each electrode. For euphony the simple word "potential" is often used, to signify the *difference of potential* existing at the interface between electrode and solution.

(1) $Zn \mid Zn^{\cdot\cdot} \mid Cu^{\cdot\cdot} \mid Cu = 1{\cdot}096$ volts

(2) $Zn \mid Zn^{\cdot\cdot} \mid Ag^{\cdot} \mid Ag = 1{\cdot}547$ volts

(3) $Cu \mid Cu^{\cdot\cdot} \mid Ag^{\cdot} \mid Ag = 0{\cdot}436$ volts

Now if the three half-cells

$Zn \mid Zn^{\cdot\cdot}$

$Cu \mid Cu^{\cdot\cdot}$

and $Ag \mid Ag^{\cdot}$

keep the same value in all possible combinations, the E.M.F. of cell (3) should be the difference of the E.M.F.s of cells (1) and (2). Actually the E.M.F. of cell (3) is found to be 0·436 volts, whilst the difference of (1) and (2) is

$$1{\cdot}547 - 1{\cdot}096 = 0{\cdot}451 \text{ volts.}$$

Although the agreement is not absolute, we obtain approximately the result expected; the same approximate agreement may be found if the E.M.F.s of other trios of reversible cells are compared, and justifies the conclusion that the potential of a given "half-cell" can be regarded as a fixed value, independent of the other half-cell with which it is combined.

It should, however, be mentioned here that in regarding the E.M.F. of the Daniell cell,

$$Zn \mid ZnSO_4 \mid CuSO_4 \mid Cu$$

as made up of the P.D.s at the interfaces

$Zn \mid \begin{array}{l} ZnSO_4 \\ \text{solution} \end{array}$

and $\begin{array}{r} CuSO_4 \\ \text{solution} \end{array} \mid Cu$

we are neglecting the possibility of a P.D. at the interface

$$\begin{array}{r|l} ZnSO_4 & CuSO_4 \\ \text{solution} & \text{solution} \end{array}$$

existing where the two solutions meet in the pores of the porous pot. This matter has been studied in some detail and it is found that in many cases the P.D. at the liquid interface is small enough to be neglected, especially where the mobility of the various ions present in the two liquids is nearly the same, and the concentrations are also similar on both sides of the boundary. Under certain conditions, however, the P.D. at the liquid junction becomes quite high, and a serious error will be caused if it is not allowed for.[1]

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[1] N. T. M. Wilsmore, *Zeitsch. Phys. Chem.* **35** (1900), 291.

Standard Electrodes. "Normal Calomel" and "Hydrogen" Scales of Potential. Having considered these possible objections, we can go on to express the potentials of the various half-cells of the type

Metal | Metallic salt solution

on some definite scale. But first it is necessary to adopt some definite "half-cell" as a "standard electrode," which can provisionally be regarded as providing zero P.D.; for the measurement of the E.M.F. of a Daniell-type cell does not tell us the absolute potential of either electrode (or half-cell), but only the difference between the two single potentials.

It would of course be possible to take the half-cell

$Zn \mid Zn^{\cdot\cdot}$

as a standard electrode; if this is called zero, $Cu \mid Cu^{\cdot\cdot}$ must be called 1·096 volts and $Ag \mid Ag^{\cdot}$ will be 1·547 volts. Alternatively, we could call $Cu \mid Cu^{\cdot\cdot}$ zero, and in that case $Zn \mid Zn^{\cdot\cdot}$ would become – 1·096 volts, and $Ag \mid Ag^{\cdot}$ would be + 0·436 volts. But in practice neither of these half-cells are sufficiently constant for general employment as "standard electrodes."

A very convenient "standard electrode," which is commonly employed in practice, is known as the "**normal calomel electrode.**" It consists of the combination

Hg | Normal KCl solution saturated with HgCl

A useful form is shown in Fig. 77. Mercury is contained in the bottom of the vessel A, and is covered with a paste of calomel, or mercurous chloride, a somewhat insoluble salt, in a normal solution of potassium chloride; the upper portion of the vessel, as well as the limb B, is filled with normal potassium chloride solution saturated with calomel. The limb D is filled with a suitable "connecting solution" which serves to connect the potassium chloride solution to the other half-cell with which the calomel electrode is to be combined, and the funnel E and three-way tap C allows the connecting solution to be renewed each time the electrode is used. The connecting fluid is chosen so as to make the P.D. at the interface between the different solutions as small as possible.

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[1] See W. C. McC. Lewis, "System of Physical Chemistry," Vol. II (Longmans, Green), 1920 edition, pp. 168–173.

The normal potassium chloride and the connecting solution meet in the annulus of the glass tap C, which must be kept free from grease. The resistance imposed by the tap is very high, but this is actually an advantage since it prevents any danger of a high current passing through the electrode, which might be prejudicial to the constancy of the potential.

If, for instance, the connecting solution used is potassium chloride, and the end of the tube D is placed in a vessel containing zinc chloride, in which a zinc electrode is immersed, the combination forms the complete cell

$$\mathrm{Zn} \mid \mathrm{ZnCl_2} \mid \mathrm{KCl} \left| \begin{array}{l}\text{KCl saturated}\\ \text{with HgCl}\end{array} \right| \mathrm{Hg}$$

The E.M.F. of the combination can be measured on the potentiometer. Suppose the value found is 1·084 volts, the zinc functioning as the negative pole. Then, if we agree to treat the normal calomel electrode as a standard electrode of zero potential, and neglect the P.D.s at the boundaries where the different solutions meet, the value of the single electrode (or half-cell)

$$\mathrm{Zn} \left| \begin{array}{l}\mathrm{ZnCl_2}\\ \text{solution}\end{array} \right.$$

is $-1·084$ volts on the "normal calomel scale."

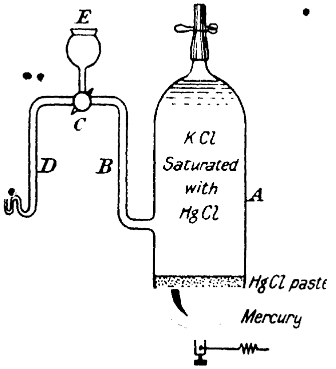

FIG. 77.—Calomel Electrode.

Another standard electrode is the **hydrogen electrode.** This consists of platinum foil, the surface of which is coated with platinum black, immersed in acid of normal hydrion concentration; during use hydrogen gas is bubbled over the metallic surface so as to keep the platinum black fully saturated with hydrogen.

When the normal calomel electrode and hydrogen electrode are combined together to form a complete cell,[1]

$$(\mathrm{Pt})\mathrm{H_2} \left| \begin{array}{c}\mathrm{HCl}\\ \text{(Normal}\\ \text{Hydrion)}\end{array} \right| \begin{array}{c}\mathrm{N}\\ \mathrm{KCl}\end{array} \left| \begin{array}{l}\mathrm{N}\\ \mathrm{KCl}\\ \text{sat. with}\\ \mathrm{HgCl}\end{array} \right| \mathrm{Hg}$$

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[1] N. T. M. Wilsmore, *Zeitsch. Phys. Chem.* **35** (1900), 291. See also G. N. Lewis, T. B. Brighton and R. L. Sebastian, *J. Amer. Chem. Soc.* **39** (1917), 2245.

the E.M.F. of the combination may be found on the potentiometer to be 0·283 volts; the hydrogen electrode functions as the negative pole. Therefore, the potential of the hydrogen electrode, on the "normal calomel scale," is $-0·283$ volts. If, however, the hydrogen electrode is regarded as the standard electrode of zero potential, the calomel electrode must be assigned a potential of $+0·283$ volts on the "hydrogen scale."

Any P.D. expressed on the "normal calomel scale" can be converted to the "hydrogen scale" by adding $+0·283$ volts. Thus the electrode

$$Zn \mid ZnCl_2$$

was stated above to be $-1·084$ volts expressed on the calomel scale; to express it on the hydrogen scale we add $+0·283$ volts, and the result is

$$-1·084 + 0·283 \text{ volts} = -0·801 \text{ volts}.$$

The calomel electrode is rather more easy to use than the hydrogen electrode, but the hydrogen scale is preferable for the expression of electro-chemical ideas. It is often convenient to measure the potential of any half-cell under investigation by coupling it with a calomel electrode, and then to convert the result obtained to the hydrogen scale by adding $+0·283$ volts. **All the values for single electrode potentials used in this book refer to the hydrogen scale unless otherwise stated.**

Some experimenters prefer to work with the "decinormal calomel electrode," which consists of the combination,

$$Hg \left| \begin{array}{l} \frac{N}{10}\,KCl \\ \text{saturated with} \\ \;\;HgCl. \end{array} \right.$$

This has a slightly different potential from the normal calomel electrode, namely $+0·338$ volts on the hydrogen scale[1]; values obtained against this electrode can be converted to the hydrogen scale by adding $+0·338$ volts. For special experimental purposes the following three electrodes are also used; the potential of each electrode is shown, expressed on the hydrogen scale. The first two[2] are useful for work with acids, the last[3] for work with alkaline solutions.

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[1] F. Auerbach, *Zeitsch. Elektrochem.* 18 (1912), 13; N. E. Loomis and S. F. Acree, *Amer. Chem. J.* 46 (1911), 585.

[2] L. Sauer, *Zeitsch. Phys. Chem.* 47 (1904), 146.

[3] F. G. Donnan and A. J. Allmand, *Trans. Chem. Soc.* 99 (1911), 845.

Hg | N HCl saturated with HgCl	P.D. = + 0·283 volts
Hg | N H_2SO_4 saturated with Hg_2SO_4	P.D. = + 0·685 volts
Hg | N NaOH saturated with HgO	P.D. = + 0·114 volts

The relationship between the values of the “normal calomel” and “hydrogen” scales are shown at a glance in Fig. 78, in which the scales are printed side by side, in the same way as Fahrenheit and Centigrade scales are often shown side by side on a thermometer. The figure also shows the potentials of some other electrodes, many of which will be referred to later.

“Absolute Potential Difference.” A third scale of Potential will be noticed in Fig. 78 side by side with the “hydrogen” and “normal calomel” scales. This is the so-called **“absolute scale,”** which is believed by many electrochemists to represent the true P.D. existing between the metal and solution.[1] The reliability of the numbers as an absolute measure of potential is, however, open to criticism, and the scale is not largely used. The principles upon which the so-called “absolute values” for the potential have been obtained can only be suggested very briefly.

The determination of the absolute potential depends on the variation of the interfacial tension of mercury with the electrification of the surface. The reluctance of mercury to enter a capillary tube is well known; it is seen when a U-tube having the one limb of narrower bore than the other is partly filled with mercury; the mercury always stands at a lower level in the narrow limb than in the broad limb. This is attributed to the surface tension of the mercury, a contractile force acting along the surface of the metal and tending to reduce the surface area to a minimum. If the surface of the mercury is electrified, an electrostatic repulsive force exists between the different portions of the charge on the surface and tends to make the surface expand, thus decreasing the effect of the surface tension. We may expect the apparent interfacial tension between mercury and any solution—as measured by any ordinary method—to be a maximum when there is no electrical P.D. at the interface.

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[1] W. Ostwald, *Zeitsch. Phys. Chem.* **35** (1900), 333; E. Newbery, *Trans. Chem. Soc.* **107** (1915), 852. See also H. G. Möller, *Zeitsch. Phys. Chem.* **65** (1909), 250.

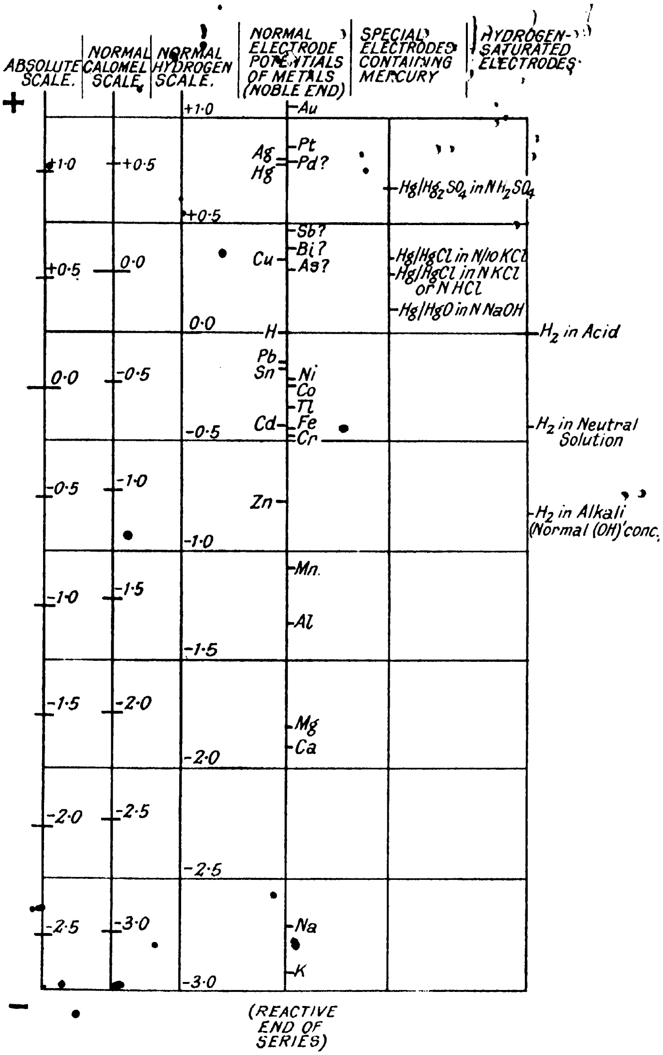

Fig. 78.—Relationship between Scales of Single Electrode Potentials.

The application of the principle to the determination of absolute potential is carried out by means of the apparatus shown in Fig. 79.[1]

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[1] See V. Rothmund, *Zeitsch. Phys. Chem.* **15** (1894), 1.

The vessel A contains mercury at the bottom, above which comes normal hydrochloric acid saturated with calomel; into the acid dips the tube B, the lower end of which has been drawn out to a fine capillary; this tube also contains mercury. The mercury in the vessel and in the tube are respectively connected to a source of variable P.D. (e.g. a potentiometer). The manometer DE contains paraffin oil, and the reservoir C contains mercury. By raising or lowering the reservoir C, it is possible to increase or decrease the pressure of the air above the mercury in B; the pressure may be measured accurately by noting the levels of the oil in the two limbs D and E of the manometer. Before the experiment commences, the mercury in the tube B does not quite reach the point of the capillary, owing to interfacial tension; its exact position can be adjusted by raising or lowering the mercury reservoir C. Any alteration in the interfacial tension will cause a movement of the mercury in the capillary, which can be observed by means of a microscope; the mercury can, however, be restored to the original position by raising or lowering C; the increase or decrease in the pressure (as measured by the movement of the oil in the manometer tubes D and E) needed to produce this restoration is a convenient measure of the alteration of the interfacial tension.

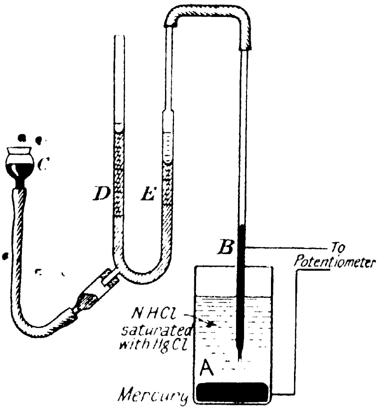

Fig. 79.—The Determination of the Absolute Value of the Potential.

Now when a small P.D. is applied to the apparatus, the interfacial tension is found to increase or decrease, according to the direction of the applied P.D. If the mercury in the tube is joined to the negative side of the source of P.D., the interfacial tension is increased; as the applied P.D. is increased in magnitude, the interfacial tension continues to increase slowly, until when the applied P.D. becomes 0·56 volts, a maximum value for the interfacial tension is obtained, and any further increase causes the interfacial tension to diminish once more.

If we are right in thinking that the P.D. at the position of maximum interfacial tension is zero, it is clear that the local P.D. at the surface of the mercury in the tube B is zero, when the total applied P.D. is 0·56 volts. In that case, the true or "absolute" value of the P.D. at the surface of the mercury in the vessel A is evidently 0·56 volts. In other words, the potential of the half-cell

$\mathrm{Hg}\left|\begin{array}{l}\mathrm{N\ HCl}\\ \text{sat. with HgCl}\end{array}\right.$ is + 0·56 volts, on the "absolute scale."

Having obtained the potential of this one standard electrode on the absolute scale, it is easy to convert the potentials of other "half-cells" to the absolute scale; for we know that the P.D. at the electrode

$\mathrm{Hg}\left|\begin{array}{l}\mathrm{N\ HCl}\\ \text{sat. with HgCl}\end{array}\right.$ is + 0·283 volts, on the "hydrogen scale."

Evidently, therefore, to convert a potential expressed on the hydrogen scale to the absolute scale, we have to add

0·56 − 0·283 volts = 0·277 volts.

The "absolute potential" of the hydrogen electrode is, according to this argument, + 0·277 volts; that of the normal calomel electrode is + 0·56 volts.

The fact that the interval between the zero points on the "absolute" and "hydrogen" scale (0·277 volts) is so nearly equal to the interval between the zero points of the "hydrogen" and "calomel" scales (0·283 volts) is worthy of notice, although it is purely a coincidence.

There are, however, certain difficulties in accepting the view that the absolute potential of a mercury electrode is necessarily zero under conditions of maximum interfacial tension. For instance, the interfacial tension of mercury appears to reach a maximum value at a slightly different potential according as it is immersed in potassium chloride or potassium iodide.[1] Since both these potentials cannot represent absolute zero, it becomes doubtful whether in either case the zero potential lies exactly at the point of maximum interfacial tension. In other instances, the discrepancy may be far more serious. Certain dye-stuffs, if added to the liquid towards which the interfacial tension of mercury is being examined, cause a marked change in the potential at which the interfacial tension reaches a maximum value, although these dyes do not affect the E.M.F. of a cell containing a mercury electrode.

One plausible explanation is that although the superficial electric charge at the mercury surface itself may be zero under conditions of maximum interfacial tension, there will, nevertheless, be a small potential difference existing over the liquid layer next to the mercury surface, due to preferential adsorption of either anions or cations.[1] The discrepancy becomes very serious in the presence of such substances as dye-stuffs which are strongly adsorbed. In the case of solutions of ordinary salts such as potassium chloride the discrepancy may not be large, and the position of maximum interfacial tension probably represents approximately the conditions of zero potential. However, until the matter is finally settled, it is preferable to use the "hydrogen scale" of potential, and not the so-called "absolute scale," for all practical purposes.

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[1] S. W. J. Smith, *Phil. Trans.* **193** [A] (1900), 47.

Before leaving the subject of the varying interfacial tension of mercury, it is well to refer to the practical employment of the principle in the "**capillary electrometer.**" The apparatus just described (Fig. 79) can, of course, be used to detect a small P.D., the direction of movement of the mercury in the capillary indicating the sign of the P.D. in question; clearly, however, the form of apparatus is not a convenient one. Various more portable forms have been devised, and that illustrated in Fig. 80 has certain advantages.[2] The mercury in the left limb A of the H-tube is covered with dilute sulphuric acid, which meets the mercury from the right-hand limb B in the horizontal capillary tube C. By means of the platinum contacts E and F and the key K the electrometer is joined to the points between which it is desired to detect a P.D.

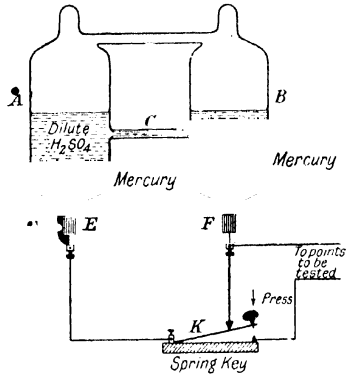

FIG. 80.—Portable Capillary Electrometer.

If a small P.D. exists between these points, a movement of mercury takes place in the capillary when the key is depressed; this movement can be observed in a microscope, or even an ordinary lens, the direction indicating the direction of the P.D. When the mercury has come to rest, practically no current flows through the apparatus, so long as the P.D. applied is small—well below the decomposition voltage of water. Thus the apparatus becomes equivalent to a sensitive milli-voltmeter of extremely high resistance. The high apparent resistance is a great advantage, and—as stated in the last chapter—many electrochemists prefer to use a capillary electrometer instead of a galvanometer as a detector or "null instrument" in potentiometer work.

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[1] H. Freundlich and P. Rona, *Sitzungsber. Preuss. Akad.* (1920), 397; H. Freundlich and M. Wreschner, *Koll. Zeitsch.* **28** (1921), 250; G. Gouy, *Annales Physique*, **7** (1917), 129; A. Frumkin, *Phil. Mag.* **40** (1920), 363, 375.

[2] S. W. J. Smith, *Phil. Mag.* **5** (1903), 398. Smith also recommends a special "mercury key" which is not shown in Fig. 80.

In spite of the fact that the current flowing through the electrometer is very small, a certain accumulation of decomposition products at the two mercury surfaces would occur in time and this might cause a back E.M.F. which would vitiate the results given by the instrument. To avoid this, the special form of spring-key, K, is employed, which "short-circuits" the electrometer as soon as the pressure of the fingers is released; thus any minute accumulation of decomposition products is at once used up, and the electrometer will "start fresh" next time the key is depressed.

Table of Normal Electrode Potentials. The table given on page 325 shows, upon the "hydrogen," "calomel" and "absolute" scales, the "normal electrode potentials" of each of the commoner metals, that is the P.D. existing—in a state of equilibrium—between the metal electrode and a solution containing normal concentration of metallic ions. The values are also shown, more roughly, in Fig. 78. In the case of many of the metals, the "normal electrode potential" has been determined by direct measurement against a calomel electrode or against a hydrogen electrode; in the case of a few metals, notably those like potassium which decompose water, less direct methods have been employed.

It will be noticed that all the highly "**reactive**" metals which are readily attacked by water and by acids stand at the bottom of the table, having negative values; on the other hand, "**noble**" metals, which are only with difficulty dissolved by acids, and which are readily reduced to the metallic condition, stand at the head of the table with high positive values. In subsequent chapters it will be shown that the value of the normal electrode potential is in many ways an *epitome* of the chemical behaviour of the metal.

The **Convention** regarding the employment of negative and positive signs should be carefully noted. **The reactive metals, such as zinc or cadmium, which usually form the negative pole of an electric battery, are assigned a negative potential; the noble metals, such as silver or platinum, which are suitable for forming the positive pole of a cell, are assigned a positive potential.** This rule is now very generally adopted in all countries, but it is worth while to warn the reader that, in many of the older papers, the opposite rule is adopted—zinc is given a positive potential and platinum a negative potential. This lack of uniformity has in the past given rise to much confusion.[1]

It is also necessary to point out that the reactive metals, with negative values for the normal electrode potentials, are often referred to as "electropositive substances"; the term implies that they readily enter the condition of a positive ion. The word "electropositive" is, perhaps, unfortunate, but there is no other which exactly expresses the same idea, and it is impossible altogether to avoid the use of it.

It should be pointed out that the normal electrode potential of a metal varies somewhat according to the surface of the metal—whether rough or polished—and that the potential of a cold-worked sample differs appreciably from that of the same sample after annealing.

Effect of Concentration.[2] The value of the equilibrium P.D. at the interface

Metal electrode | Solution containing metallic ions

will necessarily depend upon the concentration of the ions. For equilibrium implies that the two opposed reactions of the type

$$\begin{aligned} & \mathrm{M} = \mathrm{M}^{\cdot\cdot} + 2e \\ \text{and}\qquad & \mathrm{M}^{\cdot\cdot} + 2e = \mathrm{M} \end{aligned}$$

are occurring with equal velocity. Now the second of these reactions will depend on the concentration of the ions in the solution. If the ionic concentration is reduced—that is, if the solution is diluted with water—the tendency of metallic ions to pass into the metallic condition is reduced. In other words, the potential becomes lower (or, if it is already a negative value, more negative still), when the solution is diluted. All the values for the potentials quoted in the table opposite refer to "normal concentration" of ions; if the concentration of the solution is other than normal, the potential is altered by an amount equal to

$$\frac{\mathrm{RT}}{n} ln_e \mathrm{C},$$

which at room temperature (18° C.) is equivalent to

$$\frac{0{\cdot}058}{n} \log_{10} \mathrm{C} \text{ volts},$$

where n is the valency of the metal, and C the concentration of the

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[1] For the history of the rules observed regarding the sign, see W. D. Bancroft, *Trans. Amer. Electrochem. Soc.* **33** (1918), 79.

[2] See W. C. D. Whetham, "Theory of Solution" (Cambridge University Press).

TABLE OF NORMAL ELECTRODE POTENTIALS

	Hydrogen Scale.	Normal Calomel Scale.	So-called "Absolute" Scale.
Gold[1]	> +1·08	> +0·80	> +1·36
Platinum[1]	> +0·86	> +0·58	> +1·14
Palladium[1]	> +0·79	> +0·51	> +1·07
Silver[15]	+0·7987	+0·5157	+1·0757
Mercury[14] (in mercurous salts)	+0·7928	+0·5098	+1·0698
Antimony[1]	> +0·47	> +0·19	> +0·75
Bismuth[1]	> +0·39	> +0·11	> +0·67
Arsenic[1]	> +0·29	> +0·01	> +0·57
Copper[13] (in cupric salts)	+0·3469	+0·0639	+0·6239
Hydrogen (atmospheric pressure)	+0·000	−0·283	+0·277
Lead[2]	−0·132	−0·415	+0·145
Tin[3] (in stannous salts)	−0·146	−0·429	+0.131
Nickel (active)[4]	−0·20	−0·48	+0·08
Cobalt (active)[1]	−0·23	−0·51	+0·05
Thallium[12] (in thallous salts)	−0·34	−0·62	−0·06
Cadmium[1]	−0·420	−0·703	−0·143
Iron[5] (active in ferrous salts)	−0·43	−0·71	−0·15
Chromium[6] (active)	−0·47	−0·75	−0·19
Zinc[7]	−0·770	−1·053	−0·493
Manganese[1]	−1·08	−1·36	−0·80
Aluminium[8]	−1·337	−1·620	−1·060
Magnesium[10] (approx.)	−1·8	−2·1	−1·5
Calcium[9] (approx.)	−1·9	−2·2	−1·[illegible]
Sodium[10]	−2·715	−2·998	−2·438
Potassium[11]	−2·925	−3·208	−2·648

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[1] N. T. M. Wilsmore, *Zeitsch. Phys. Chem.* **35** (1900), 318.

[2] W. E. Henderson and H. Stegeman, *J. Amer. Chem. Soc.* **40** (1918), 84. A slightly different value is given by F. H. Getman, *J. Amer. Chem. Soc.* **40** (1918), 611.

[3] A. A. Noyes and K. Toabe, *J. Amer. Chem. Soc.* **39** (1917), 1537.

[4] A. Smits and C. A. Lobry de Bruyn, *Proc. Amst. Acad.* **20** (1917–18), 394. Similar values were obtained by E. P. Schoch, *Amer. Chem. J.* **41** (1909), 208, who gives a satisfactory explanation of the divergent values obtained by earlier workers.

[5] T. W. Richards and G. E. Behr, *Zeitsch. Phys. Chem.* **58** (1907), 301.

[6] A. H. W. Aten, *Proc. Amst. Acad.* **20** (1917–18), 812.

[7] N. T. M. Wilsmore, *Zeitsch. Phys. Chem.* **35** (1900), 318; W. Kistiakowsky, *Zeitsch. Elektrochem.* **14** (1908), 113. Compare W. C. Moore, *J. Amer. Chem. Soc.* **43** (1921), 81.

[8] J. Heyrovsky, *Trans. Chem. Soc.* **117** (1920), 27.

[9] L. Cambi, *Atti. R. Accad. Lincei*, **23** (1914), ii. 606; **24** (1915), i. 817, 932. Compare R. P. Beck, *Rec. Trav. Chim.* **41** (1922), 353; W. Kistiakowsky, *Zeitsch. Elektrochem.* **14** (1908), 113.

[10] G. N. Lewis and H. A. Kraus, *J. Amer. Chem. Soc.* **32** (1910), 1459.

[11] G. N. Lewis and F. G. Keyes, *J. Amer. Chem. Soc.* **34** (1912), 119.

[12] G. N. Lewis and G. L. von Ende, *J. Amer. Chem. Soc.* **32** (1910), 732. T. W. Richards and C. P. Smyth, *J. Amer. Chem. Soc.* **44** (1922), 524.

[13] G. N. Lewis and W. N. Lacey, *J. Amer. Chem. Soc.* **36** (1914), 804.

[14] G. A. Linhart, *J. Amer. Chem. Soc.* **38** (1916), 2356.

[15] F. J. Brislee, *Trans. Faraday Soc.* **4** (1908), 159. Compare I. M. Kolthoff, *Zeitsch. Anorg. Chem.* **119** (1921), 202, who finds values 0·01 volts lower.

solution expressed in gram-molecules per litre; for a normal solution $C = 1$, and the total alteration becomes zero.

The meaning of the logarithmic expression just given can be expressed in a very simple way. Whenever we dilute the solution surrounding an electrode so as to reduce the ion concentration to one tenth of its former value, we shift the potential by $\frac{0 \cdot 058}{n}$ volts. Thus if we start with a half-cell consisting of a silver electrode in normal silver nitrate

$$\text{Ag} \mid \text{N AgNO}_3 \text{ with a P.D. about } + 0 \cdot 799 \text{ volts}$$

and dilute the silver nitrate solution to one-tenth of the former concentration, so that we obtain the half-cell

$$\text{Ag} \mid \frac{\text{N}}{10} \text{AgNO}_3$$

we ought to reduce the P.D. by about 0·058 volts (since for silver, $n = 1$). Actually it falls by a slightly smaller amount, since the ionization of N $AgNO_3$ is rather less complete than that of $\frac{N}{10}$ $AgNO_3$. If we again dilute the solution tenfold, obtaining the cell

$$\text{Ag} \mid \frac{\text{N}}{100} \text{AgNO}_3$$

we ought again to reduce the potential by about 0·058 volts. If we combine the last two half-cells, so as to obtain the complete cell

$$\text{Ag} \mid \frac{\text{N}}{10} \text{AgNO}_3 \mid \frac{\text{N}}{100} \text{AgNO}_3 \mid \text{Ag},$$

the combination ought to produce an E.M.F. of 0·058 volts, assuming that the P.D. between the two solutions can be neglected. Nernst found by experiment that the combination balances a P.D. of 0·055 volts—a sufficiently good agreement.[1]

A cell of this kind is known as a **concentration cell**; it will be obvious that the E.M.F. provided by a concentration cell will always be a low one unless the difference between the concentrations in the two halves is very great. The provision of a very low but constant concentration of silver ions in the "low concentration" half of the cell is conveniently obtained by keeping a sparingly soluble salt in suspension. For instance, a solution of potassium chloride containing silver chloride in suspension has a concentration of silver ions considerably less than ·000011 normal, and the potential of the half-cell

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[1] W. Nernst, "Theoretical Chemistry"; translation by H. J. Tizard (Macmillan), 1916 edition, p. 800.

$$\mathrm{Ag} \left| \begin{array}{l} \text{KCl saturated} \\ \text{with AgCl} \end{array} \right.$$

therefore differs very much from that of the half-cell

$$\mathrm{Ag} \mid \mathrm{N\ AgNO_3}\ \text{solution}$$

or the half-cell $\mathrm{Ag} \left| \frac{\mathrm{N}}{10} \mathrm{AgNO_3} \right.$.

In fact, by combining it with one of these half-cells, we obtain a cell

$$\mathrm{Ag} \left| \begin{array}{l} \text{KCl saturated} \\ \text{with AgCl} \end{array} \right| \frac{\mathrm{N}}{10} \mathrm{AgNO_3} \mid \mathrm{Ag}$$

which, although both electrodes are composed of the same metal, balances a P.D. as high as 0·52 volts.

It is the concentration of metallic *ions* which is of importance in determining the potential, not the total concentration of metal in solution. This is shown by the behaviour of a metallic electrode immersed in a solution of a complex salt. Contrast the potentials of the following half-cells[1]:—

$$\left.\begin{array}{lr} \mathrm{Ag} \left| \frac{\mathrm{N}}{4} \mathrm{AgNO_3} \right. & +\ 0{\cdot}76\ \text{volts} \\ \mathrm{Ag} \left| \frac{\mathrm{N}}{4} \mathrm{AgCN.KCN} \right. & +\ 0{\cdot}15\ \text{volts} \\ \mathrm{Ag} \left| \frac{\mathrm{N}}{4} \mathrm{AgCN.KCN} + \frac{\mathrm{N}}{4} \mathrm{KCN} \right. & -\ 0{\cdot}37\ \text{volts} \end{array}\right\} \begin{array}{l} \text{(approximate} \\ \text{values only)} \end{array}$$

In all three cases there is the same amount of silver in solution, but in the first case it exists as ordinary metal cations, whilst in the complex cyanide solution it exists, for the most part, as the complex anion $[\mathrm{Ag(CN)_2}]'$. The concentration of $\mathrm{Ag^{\cdot}}$ ions is very small, especially in the last case, where potassium cyanide is present in excess; hence the P.D. is shifted to a marked extent in the negative direction.

The alteration in the potential of copper caused by the presence of cyanide in solutions is shown by the following striking experiment. When the ordinary Daniell cell

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{CuSO_4} \mid \mathrm{Cu}$$

yields a current, the zinc acts as the attackable (negative) electrode.

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[1] Founded on data given by F. C. Frary and R. E. Porter, *Trans. Amer. Electrochem. Soc.* **28** (1915), 307.

But if in the place of copper sulphate a solution of potassium cyanide is used, so as to produce the cell

$$Zn \mid ZnSO_4 \mid KCN \mid Cu$$

the copper becomes the attackable (negative) electrode, and zinc is forced out of solution. The current produced therefore passes in the opposite direction.[1]

This is an explanation of the fact that, towards cyanide solutions, "noble" metals like gold, silver and copper—which withstand the action of ordinary reagents so well—behave as quite easily attacked substances. In the cyanide solutions these metals exist, not as cations, but as complex anions.

Electrode Potential of Hydrogen. Of all the elements mentioned in the table of normal electrode potentials, hydrogen alone is not a metal. The so-called hydrogen electrode, the potential of which is taken as zero on the "hydrogen scale," consists of blackened platinum saturated with hydrogen under one atmosphere pressure and immersed in a solution containing normal concentration of hydrogen ions (e.g. 1·3 N hydrochloric acid, or 2·1 N sulphuric acid).

The case is of especial interest because not only can we vary the concentration of hydrogen in the electrode, by saturating the platinum under a pressure of hydrogen greater or less than one atmosphere, but we can also—alternatively—vary the concentration of hydrogen ions in the solution, by altering the acidity of the liquid employed. Either of these variations will cause the equilibrium P.D. to depart from zero.

For the existence of equilibrium demands that the two opposite reactions

$$(1)\qquad H_2 \rightarrow 2H^{\cdot} + 2e$$

and

$$(2)\qquad 2H^{\cdot} + 2e \rightarrow H_2$$

should occur with equal velocity. Now if the concentration of hydrogen in the electrode is increased, change (1) is favoured. The equilibrium potential is therefore made negative by any excess of pressure of the hydrogen gas used to saturate the electrode, but is made positive if a pressure below one atmosphere is employed; this has been experimentally verified by different observers.[2]

The alteration caused by varying the hydrion concentration of the solution is far more striking, because a greater variation can conveniently be brought about. For high concentrations of hydrion, solutions containing acid are used. But even pure water—quite free from acid—is to a very small extent ionized, according to the equation

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[1] See W. Hittorf, *Zeitsch. Phys. Chem.* **10** (1892), 592. For further details of the effect of cyanide on the potential of copper, see F. Spitzer, *Zeitsch. Elektrochem.* **11** (1905), 345, 391.

[2] G. N. Lewis and M. Randall, *J. Amer. Chem. Soc.* **36** (1914), 1969; J. H. Ellis, *J. Amer. Chem. Soc.* **38** (1916), 737; N. E. Loomis and S. F. Acree, *J. Amer. Chem. Soc.* **38** (1916), 2391; W. R. Hainsworth and D. A. MacInnes, *J. Amer. Chem. Soc.* **44** (1922), 1021.

$$H_2O \rightleftharpoons H^{\cdot} + OH'$$

and therefore contains hydrion. The concentration of hydrion in pure water is about 10^{-7}N, but it is still further diminished by the addition of alkaline substances containing free hydroxyl ions to the water—as would be expected from the Law of Mass Action; a normal solution of alkali has a hydrion concentration of about 10^{-14}N.

The variation in the potential of the platinum saturated with hydrogen at atmospheric pressure and immersed in liquids of varying hydrion concentration at 18° C. can be calculated from the equation

$$E = \frac{0{\cdot}058}{n} \log C.$$

Since for hydrogen $n = 1$, this becomes

$$E = 0{\cdot}058 \log C.$$

For 1·3 N hydrochloric acid, the hydrion concentration is normal, and $C = 1$, $\log C = 0$
For neutral water, $C = 10^{-7}$, $\log C = -7$
For normal alkali, $C = 10^{-14}$, $\log C = -14$

Hence we have for the electrodes:—

Pt, H_2	Concentrated acid (above normal hydrion concentration).	P.D. is positive.
Pt, H_2	1·3 N. Hydrochloric acid (normal hydrion concentration).	P.D. = 0·000 volt.
Pt, H_2	Neutral water.	$P.D. = -7 \times 0{\cdot}058 = -0{\cdot}406$ volt.
Pt, H_2	Normal alkali.	$P.D. = -14 \times 0{\cdot}058 = -0{\cdot}812$ volt.

The following cell, which can be regarded as a hydrion concentration cell, furnishes a P.D. of 0·83 volt:—

Pt saturated with hydrogen	Acid of normal hydrion concentration	Alkali of normal hydroxyl concentration	Pt saturated with hydrogen

The Effect of Oxidizing Agents upon the Potential.—Many writers give tables of normal electrode potentials which include values relating to oxygen, chlorine, bromine and similar non-metals. It is, of course, impossible to prepare electrodes from these materials, but they can exist adsorbed upon the surface of an unattackable electrode—such as platinum—or dissolved in the solution in which the electrode is immersed.

The presence of oxygen in an electrode always renders the potential more positive—that is, it renders the metal more noble. Certain metals, such as iron and nickel, which are moderately reactive under ordinary circumstances, acquire comparatively "noble" properties when they contain oxygen.

The presence of bromine or iodine in the liquid surrounding a platinum electrode also renders the potential somewhat more positive. The same is true of the various soluble oxidizing agents, such as potassium permanganate, which can be regarded as equivalent to oxygen acting under high pressure. The potential of a platinum electrode immersed in a solution of an oxidizing agent can be regarded as an indication of the vigour of the oxidizing agent, as is shown in the table below.[1]

Various reducing agents—substances which can be regarded as equivalent to hydrogen under pressure—are included in the table for the sake of completeness; reducing agents naturally tend to make the potential of platinum less positive.

Name of Oxidizing Agent or Reducing Agent in Solution.	P.D. at Platinum Electrode (Hydrogen Scale).
Oxidizing agents :—	
Potassium permanganate	+ 1·48
Chlorine in acid solution	+ 1·39
Potassium iodate	+ 1·21
Bromine in potassium bromide	+ 1·15
Chromic acid	+ 1·12
Nitric acid	+ 0·98
Ferric chloride	+ 0·96
Chlorine in alkaline solution	+ 0·86
Potassium dichromate	+ 0·78
Iodine in potassium iodide	+ 0·61
Reducing agents :—	
Ferrous sulphate in acid	+ 0·50
Sulphurous acid	+ 0·44
Ferrous sulphate, neutral	+ 0·35
Potassium arsenite	+ 0·23
Stannous chloride in acid	+ 0·22
Hydrogen in acid	+ 0·00
Chromous acetate in alkali	– 0·31
Stannous chloride in alkali	– 0·58

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[1] Further examples are given by W. Ostwald, "Outlines of General Chemistry"; translation by W. W. Taylor (Macmillan).

Electrode Potentials of Reactive Metals. Most of the metals belonging to the "A groups" of the periodic table are highly reactive substances which cannot be deposited electrolytically from an aqueous solution of the salts. In such cases the determination of the normal electrode potential presents difficulty. The electrode potential should represent the equilibrium between a metal and its ions, according to a balanced equation of the type

$$M \rightleftharpoons M^{\cdot} + e.$$

In order to ensure that the potential measured really represents this equilibrium, it is desirable to ascertain the fact that when the potential is depressed below the supposed equilibrium value, metal is actually deposited according to the equation,

$$M^{\cdot} + e = M,$$

and that, when the potential is elevated somewhat, metal passes into solution, according to the reverse change,

$$M = M^{\cdot} + e.$$

If a metal cannot be deposited from aqueous solution—as is the case with such metals as vanadium and tungsten—the significance of the equilibrium potential measured on the potentiometer becomes doubtful. Certain experimenters claim to have measured the normal electrode potential of metals of this character; but, although the accuracy of the measurements is not questioned, it is doubtful whether it represents the equilibrium

$$M \rightleftharpoons M^{\cdot} + e.$$

It may for instance represent the equilibrium

$$H \rightleftharpoons H^{\cdot} + e,$$

since there is always occluded hydrogen present at the surface of electrodes made of these metals. Furthermore, there is considerable doubt as to the concentration of cations in solutions of metallic salts of this character; it is probably mainly due to the small concentration of cations in the solutions that metals like tungsten cannot be deposited electrolytically from an aqueous solution. The published values for the normal electrode potential of such metals as tungsten—although not altogether devoid of importance—have a significance quite different from the values ascribed to such metals as copper and silver.

In the case of metals like sodium and potassium, which decompose water, values for the electrode potentials have been obtained by an indirect method, in which the amalgam is employed. Details of this method, which appears to be quite satisfactory, must be sought elsewhere.[1]

Use of Electrode Potential Measurements in Volumetric Analysis. In order to render familiar the notion of electrode potentials, it is convenient here to refer to certain applications of potentiometer work to volumetric analysis.

The ordinary method of estimating an acid solution by titration with alkali in presence of an indicator such as litmus or phenolphthalein, becomes unsatisfactory in certain cases. For instance, if the solution contains coloured substances—as is the case in many of the acid liquors used in tanning—the colour change of the indicator cannot be observed. Again, if the solution contains the salts of weak acids, the colour-change is often gradual, and there is doubt as to what point should be regarded as the end-point; frequently, different indicators show their distinctive colour changes at quite different points.

In such cases, the method of electro-titration is very helpful.[2] It depends on the variation in the potential of the hydrogen electrode according as the liquid is acid, neutral or alkaline. The normal calomel electrode is used as the second half-cell, and the E.M.F. of the combination can be calculated in the three possible cases.

Pt,H_2 | Acid | Normal Calomel electrode E.M.F. = 0·283 − 0·00 = 0·283 volts

Pt,H_2 | Neutral liquid | Normal Calomel electrode E.M.F. = 0·283 − (− 0·406) = 0·689 volts

Pt,H_2 | Alkaline liquid | Normal Calomel electrode E.M.F. = 0·283 − (− 0·812) = 1·095 volts

A useful form of the apparatus employed is shown diagrammatically in Fig. 81. The hydrogen electrode consists essentially of a piece of blackened platinum foil, P, supported by a piece of platinum wire sealed through the glass tube T. It is surrounded by the slotted glass hood H, into which hydrogen gas is passed through the side tube S. The whole is immersed in the liquid to be titrated contained in a beaker. The level of the slot is such that the liquid always covers half the surface of the platinum, and the hydrogen is introduced into the hood at such a rate that a bubble escapes from the notch every second or two; after the gas has been bubbled through the liquid for 10 minutes the platinum is saturated with hydrogen, but the bubbling should be continued throughout the titration in order to ensure that it remains saturated.

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[1] G. N. Lewis and H. A. Kraus, *J. Amer. Chem. Soc.* **32** (1920), 1459; G. N. Lewis and F. G. Keyes, *J. Amer. Chem. Soc.* **34** (1912), 119.

[2] J. H. Hildebrand, *J. Amer. Chem. Soc.* **35** (1913), 847; H. J. S. Sand and D. J. Law, *J. Soc. Chem. Ind.* **30** (1911), 3. An older method is described by W. Böttger, *Zeitsch. Phys. Chem.* **24** (1897), 253.

The end of the tube of the normal calomel electrode N is also introduced into the liquid, and the connecting leads from the two electrodes are joined to an ordinary potentiometer, which is adjusted so as to balance—and thus measure—the E.M.F. provided by the combination.

With the acid liquid placed in the beaker the combination yields at the beginning about 0·3 volts; when alkali is added gradually from the burette, the E.M.F. rises slightly, but, as long as acid is in distinct excess, the rise is but small. Just before neutrality is obtained, however, the E.M.F. rises sharply, and, when alkali is actually in excess, the combination requires a P.D. of about a volt to balance it. The "neutrality point" is taken as being the point when the P.D. is equal to 0·69 volts.

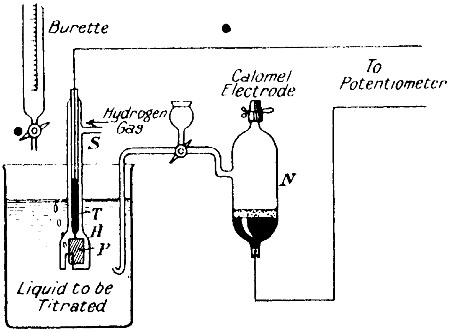

FIG. 81.—Electrometric Titration of Acid by Alkali.

When the salts of weak acids are present in the liquor to be tested, the rise of E.M.F. is less sudden, and it is easy to understand why an ordinary indicator should give a gradual colour change; with the electrical method, however, there is never any doubt about the end-point, which is always taken as the moment when the combination produces an E.M.F. of 0·69 volts.

It is possible to use the same apparatus to observe the potential at which the characteristic colour changes of different indicators occur, and from the potential the hydrion concentration which determines the colour change can easily be calculated from the equation,

$$E = 0{\cdot}058 \log C.$$

By this method, for instance, it has been found that[1]:—

Phenolphthalein turns pink when the hydrion concentration drops below 8×10^{-10}N.

Methyl orange turns from orange-red to yellowish-orange when the hydrion concentration drops below 5×10^{-4}N.

Lacmoid turns very gradually from red (at 10^{-5}N) through red-violet (10^{-6}N), violet (10^{-7}N) to blue (10^{-8}N). Litmus shows a similar gradual colour-change from red through violet to blue. The violet range corresponds to about 10^{-7}N, the hydrion concentration of pure water.

It is now clear why methyl orange is not turned distinctly red by carbonic acid; carbonic acid is a feebly ionized acid and has, moreover, a small solubility. The hydrion concentration even of the saturated solution is never as high as 5×10^{-4} normal, and therefore this acid cannot cause the colour change.

Another application of electrical methods to determine the end-point in volumetric analysis concerns the titration of oxidizing agents by reducing agents, and vice versa.[2] For instance, the estimation of ferrous iron in the presence of chlorides is nearly always carried out by titration with potassium dichromate. No marked colour change accompanies the reaction, and in ordinary practice it is necessary, after each addition of dichromate, to ascertain the progress of titration by testing a drop of the liquid with a drop of potassium ferricyanide on a porcelain slab. As long as ferrous iron remains in the solution, a blue precipitate of ferrous ferricyanide is obtained. This method, however, occupies time, and, in the presence of colloids or of coloured substances, it may be very difficult to tell when the end-point has been reached.

Here again the introduction of a calomel and platinum electrode into the solution gives a combination, the E.M.F. of which changes suddenly as the end-point of the reaction is reached. In this case, a bright platinum electrode can be employed, and there is no occasion to keep it saturated with hydrogen. The solution must be kept vigorously stirred throughout the titration. The combination

Pt | Ferrous salt | Normal Calomel Electrode

gives an E.M.F. which when measured on the potentiometer is about 0·2 volts. Potassium dichromate can now be run in from the burette. The first additions cause little change in the value of the E.M.F. As, however, the end-point is approached the E.M.F. rises rapidly, and as soon as the dichromate is present in excess, the E.M.F. of the cell, which can then be written

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[1] E. Salm, *Zeitsch. Phys. Chem.* **57** (1907), 471. See also E. B. R. Prideaux, "Theory of Indicators" (Constable).

[2] G. S. Forbes and E. P. Bartlett, *J. Amer. Chem. Soc.* **35** (1913), 1527; J. C. Hostetter and H. S. Roberts, *J. Amer. Chem. Soc.* **41** (1919), 1337; G. L. Kelley and R. T. Bohn, *J. Amer. Chem. Soc.* **41** (1919), 1776; G. L. Kelley, J. R. Adams, and J. A. Wiley, *J. Ind. Eng. Chem.* **9** (1917), 780.

Pt | Dichromate | Normal Calomel Electrode

is about 0·8 volts. It is customary to take the " end-point " as the point at which the E.M.F. becomes equal to 0·58 volts.

The method has been applied to the converse operation, the titration of chromates with ferrous iron. In this case, of course, the E.M.F. falls suddenly—instead of rising suddenly—as the end-point is approached. It has also been found useful for the titration of a vanadate solution with a ferrous solution, in the volumetric estimation of vanadium.[1]

Finally, the elevation of the potential at a platinum electrode caused by the presence of an oxidizing agent has been used for the estimation of small quantities of hypochlorites in sterilized drinking-water,[2] and also in the titration of hypochlorites, at greater concentrations, by arsenious acid.[3]

Summary. It is found possible to regard the equilibrium E.M.F. of a cell of the Daniell type as the difference between the " single potentials " of the two " half-cells " or " single electrodes ", (the P.D. at the junction between the two liquids being usually small). By choosing a given " half-cell " (e.g. the " normal calomel electrode " or the " hydrogen electrode ") as a standard, and fixing the potential of that " half-cell " as zero, we can express consistently the potentials of other single electrodes on a scale ; thus the " normal calomel " and the " hydrogen " scales—differing by 0·283 volts—are arrived at. The so-called " absolute scale " is based upon the assumption that the P.D. at a mercury surface really becomes zero, when the interfacial tension of the mercury is a maximum ; this is probably not quite true, and the " absolute scale " is seldom used.

The P.D. existing between a metal electrode and a solution of one of its salts depends not only upon the character of the metal, but upon the concentration of the ions in the solution. By determining, or calculating, the potential of a metal against a solution of normal ion concentration we get the " normal electrode potential " of the metal. We can arrange the metals in order of their " normal electrode potentials," and thus obtain a series—the " Potential Series "—in which the noble metals like gold and platinum (with high positive potentials (according to the present convention regarding signs) stand at the top, and the reactive metals like zinc and potassium (with negative potentials) stand at the bottom. The value of the normal electrode potential epitomizes the stability or reactivity of a metal.

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[1] G. L. Kelley and J. B. Conant, *J. Amer. Chem. Soc.* **38** (1916), 341.

[2] E. K. Rideal and U. R. Evans, *Analyst*, **38** (1913), 353.

[3] W. D. Treadwell, *Helv. Chim. Acta.* **4** (1921), 396.

The P.D. at a metal electrode varies with the concentration of cations in the solution, a metal becoming virtually less " noble " in a dilute solution, and especially in a solution in which it exists as complex anions instead of as normal cations. Thus silver and copper, which behave like noble metals towards an ordinary salt solution, behave like reactive metals towards cyanide solutions.

The potential of hydrogen is extremely interesting ; it varies with the concentration of hydrogen in (or upon) the electrode-material, and also with the concentration of hydrogen ions in the solution. The potential of hydrogen-saturated platinum in an alkaline solution differs by about 0·8 volts from that in an acid solution, being lower (more negative) in alkaline solution. This fact is used in the electrometric method of titrating acids by alkalis —which is convenient in coloured solutions, and in other cases where the employment of an indicator is impossible.

The potential of an insoluble electrode like platinum is rendered highly positive by the presence of an oxidizing agent in the solution, but is depressed by the presence of a reducing agent. An electrometric method of titrating oxidizers by reducers and vice versa is based upon this fact.

CHAPTER X

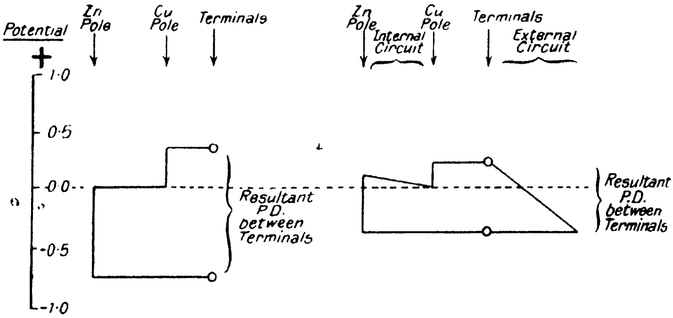
POLARIZATION AND OVERPOTENTIAL

Polarization. In the last chapters we have dealt with the potentials of cells and half-cells corresponding to equilibrium conditions; in the present chapter, it is necessary to consider how these potentials alter when current commences to flow.

It has been stated, for instance, that the electrolytic decomposition of zinc bromide commences as soon as the applied E.M.F. exceeds 1·8 volts. But, if the decomposition is to take place at any considerable rate, this critical potential must be exceeded by a considerable amount; the greater the excess potential employed, the quicker the current is pushed through the cell, and the quicker, therefore, does the decomposition occur. Part of this excess potential falls over the liquid within the cell, but a good deal is also accounted for by the fact that—when the current is increased—the potential at each electrode alters. The potential at the cathode becomes more negative than the equilibrium value of the electrode Zn | $ZnBr_2$, and the electrode is said to be **cathodically polarized**; meanwhile the potential at the anode becomes unduly positive, and the electrode is said to be **anodically polarized.**

The same sort of effect is seen in current-producing cells. Consider once more the Daniell cell. In a state of equilibrium, it balances a P.D. of 1·096 volts. But, when the Daniell cell is made to yield a current, this full E.M.F. is not necessarily obtained. If an accurate voltmeter be connected across the terminals of a Daniell cell, which is made to yield a current through an external circuit, an E.M.F. less than 1·096 volts will be registered; the lower the resistance of the external circuit is made—and the higher the current which the cell sends round that circuit—the more the E.M.F. drops below the equilibrium value.

The two causes of the drop in the E.M.F. are explained graphically in Fig. 82. In a state of equilibrium (Fig. 82 (*a*)), the full P.D. of 1·096 volts is produced, this being the algebraic difference between the single potentials at the copper and zinc poles. But when the cell furnishes current round an external circuit (Fig. 82 (*b*)), a fraction of the voltage produced falls over the electrolyte within the cell—the resistance of which is not negligible ; only the portion which falls outside the cell is registered on the voltmeter. There is, however, a second important cause for the low reading on the voltmeter. The single potentials at the two poles are no longer equal to the equilibrium values ; the zinc has become anodically polarized, and is less negative than before ; the copper has become cathodically polarized, and is less positive than before. The algebraic difference between the two is no longer 1·096 volts, and



(a) Equilibrium (Balance) (b) Current Production

FIG. 82.—Distribution of Potential in Daniell Cell Circuit (a) in state of Balance, (b) when producing Current.

the higher the current the cell is called upon to produce, the less will the E.M.F. of the combination become.

A particularly interesting case is that of the cell

Cu | $CuSO_4$ solution | Cu

Here the single potential at each electrode is—in a state of equilibrium—the same, and the combination as a whole has a critical E.M.F. equal to zero. However, when a current is forced through the cell the potentials at the two electrodes are no longer the same as before. The single potential at either copper electrode can be determined whilst the current is passing, by inserting the tube of a calomel electrode into the copper sulphate solution right against one of the copper electrodes, and joining both the calomel and the copper electrodes to a potentiometer. It is found that, when current passes, the potential at the cathode becomes less positive (cathodically polarized), whilst that at the anode becomes more positive (anodically polarized). The higher the "**current den-**

sity" (that is, the current per unit electrode area) becomes, the greater is the amount of **polarization** or departure from the equilibrium potential. The polarization of a cell of this kind corresponding to different values of the current density is shown by the curves of Fig. 83.[1] Curve C shows the cathodic polarization—the departure of the cathodic potential from the equilibrium value; curve A shows the anodic polarization, whilst curve T represents the total polarization, the arithmetic sum of the polarization at the cathode and the anode. The total E.M.F. which must be impressed upon the cell to obtain any particular current density will greatly exceed the total polarization, since it will include the potential falling over the liquid between the electrodes, the magnitude of which will depend upon the distance between the electrodes as well as upon the conductivity of the solution; the total E.M.F. for one particular cell is suggested by the curve E.

The occurrence of polarization is by no means surprising. Although a very small departure from the equilibrium potential should—at a reversible electrode—cause a slow transformation of atoms from the ionic state to the metallic state or vice versa, yet the velocity of this change will be limited.[2] As the potential is altered further from the equilibrium value, the velocity of the change increases and the current per unit area, which is a measure of the velocity of the change, increases also. To every possible value of the polarization, a definite current density corresponds.

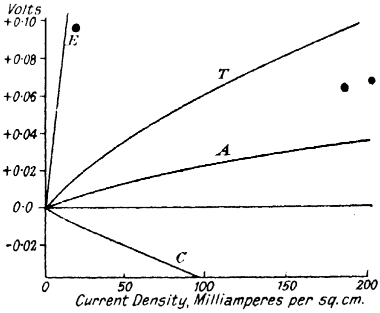


FIG. 83.—Polarization on the Cell Cu | $CuSO_4$ | Cu.

In many cases, if the current is allowed to flow through a cell for some time and is then shut off, the potential at each electrode slowly returns to the equilibrium value; but, in certain instances, the effects of polarization are comparatively permanent, the potential at the anode remaining abnormally high, and that at the cathode abnormally low, long after the current has been stopped. This is often due to the presence of gases (oxygen at the anode, hydrogen at the cathode) which have been produced by the action of the current. In other cases, the persistence of the abnormal potentials can be referred to changes in concentration around the electrodes produced by the passage of current.[1] For instance, in the cell

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[1] O. P. Watts, *Trans. Amer. Electrochem. Soc.* **19** (1911), 103. Compare also D. Reichinstein, *Zeitsch. Elektrochem.* **18** (1912), 850, who has studied the effect of acidity on the polarization of the Cu | Cu·· electrode.

[2] "Limited reactional velocity" as the primary factor in polarization is rightly insisted on by M. Le Blanc, *Zeitsch. Elektrochem.* **6** (1900), 472. Compare, however, W. Block, *Ann. Phys.* **22** (1907), 505.

$$Cu \mid CuSO_4 \mid Cu$$

referred to above, the solution next to the cathode where copper is being deposited quickly may become more or less exhausted of copper ions and that round the anode will become more concentrated than the body of the solution. These concentration changes will produce an alteration of potential at each electrode; the potential will become less positive at the cathode and more positive at the anode. The "concentration type of polarization" is of course greatly reduced by the mechanical stirring of the solution.

Marked polarization occurs at a much lower current density when complex salts are employed than when simple salts alone are present in the solution. The potential at the cathode[2]

$$Cu \mid KCN.CuCN,$$

for instance, alters much more quickly with increasing current density than the potential at the cathode[3]

$$Cu \mid CuSO_4$$

The difference is no doubt due to the comparative paucity of $Cu^{\cdot\cdot}$ or $Cu^{\cdot}$ ions in the complex salt bath, in which local exhaustion of ions readily occurs. Moreover the fact that in the cyanide bath, the current carries the copper—as a whole—away from the cathode, instead of towards it, must help in causing polarization.

"Overpotential" accompanying the Evolution of Gas.[4]

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[1] Concentration changes, due to "limited velocity of diffusion" as an important factor in polarization is well shown by the work of Nernst and his pupils. See E. Salomon, *Zeitsch. Phys. Chem.* **24** (1897), 54; **25** (1898), 365; U. Grassi, *Zeitsch. Phys. Chem.* **44** (1903), 460; W. Nernst, **47** (1904), 52; W. Nernst and E. S. Merriam, *Zeitsch. Phys. Chem.* **53** (1905), 235. Other papers worth consulting are those of F. G. Cottrell, *Zeitsch. Phys. Chem.* **42** (1903), 385; A. H. W. Aten, *Proc. Amst. Acad.* **19** (1917), 653, 765.

[2] F. Spitzer, *Zeitsch. Elektrochem.* **11** (1905), 345.

[3] G. Coffetti and F. Foerster, *Ber.* **38** (1905), 2934.

[4] Note: E. Newbery, *Trans. Chem. Soc.* **109** (1916), 1051, 1066, 1107, 1359, uses the word "overvoltage" in a sense different from that in which other workers employ it, since by means of a commutator he measures the P.D. at an electrode after the polarizing current has been shut off. He thus obtains only the permanent polarization. The reader when referring to his papers should bear this in mind. Newbery's attitude is criticized by D. A. MacInnes, *J. Amer. Chem. Soc.* **42** (1920), 2233. Practical work by S. Dunnill, *Trans. Chem. Soc.* **119** (1921), 1081 indicates that Newbery's method is less satis-

Where the electrodic reaction is such as would cause the evolution of gases upon an electrode, a special type of polarization is met with. If, for instance, a small E.M.F. is applied to an electrolytic cell filled with dilute acid, and is gradually increased, one would expect that the evolution of hydrogen gas would commence at the cathode as soon as the potential at the cathode is depressed below 0·0 volts. As a matter of fact, if the cathode consists of blackened platinum, the evolution of hydrogen in bubbles commences at a cathode potential of −0·005 volts; but, with other electrode materials, it does not begin until a far more negative point is reached; at a zinc cathode, for instance, it only commences when the potential reaches −0·7 volts. The difference between the potential at which bubble-formation commences and the true equilibrium potential is called the **overpotential**; it depends on the nature of the cathode material, and also on the character of the surface, being greater upon a smooth surface than upon a rough one. The same electrode will, however, give different overpotential values at different times, and the discrepancy between the values obtained by different experimenters who have used different methods for measuring it is very great.

The following table shows the cathodic overpotential of hydrogen evolution upon various surfaces as obtained by Caspari using an acid solution.[1] The numbers refer to "room temperature" overpotential falls off rapidly as the temperature rises.

Platinum (black)	0·005	volts	Copper	0·23	volts
Platinum (bright)	0·09	,,	Cadmium	0·48	,,
Gold	0·02	,,	Tin	0·53	,,
Silver	0·15	,,	Lead	0·64	,,
Nickel	0·21	,,	Zinc	0·70	,,
Iron (Newbery's method) about	0·2	,,	Mercury	0·78	,,

Overpotential—although a form of polarization—should be distinguished clearly from the *gradual* change in potential with increase of current density which has been discussed at the beginning of this chapter. The ordinary type of polarization, such as occurs in the deposition of copper from a sulphate bath, can—in general—

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factory than the "direct method" commonly employed. Newbery's reply to Dunnill appears in *Trans. Chem. Soc.* **121** (1922), 7.

[1] These values—except in the case of iron—are those given by W. A. Caspari, *Zeitsch. Phys. Chem.* **30** (1889), 89. See also H. Nutton and H. D. Law, *Trans. Faraday Soc.* **3** (1907), 50, for values in alkaline solution. J. Tafel, *Zeitsch. Phys. Chem.* **50** (1905), 712, has measured the cathodic P.D. at high current densities and his numbers include the effect of ordinary polarization. Other measurements have been made by A. Cochr, *Zeitsch. Phys. Chem.* **38** (1901), 609.

be made negligibly small if we are content to carry out our electrodic reaction very slowly—that is, at a very small current density; it seems essentially to be connected with the limited velocity of a chemical reaction—or the limited velocity of the diffusion of salts. But the "overpotential" which attends the evolution of a gas in bubbles is different. It cannot be overcome by working at a low velocity. Until the cathodic potential at a smooth zinc electrode, for instance, differs from the equilibrium potential by 0·70 volts, hydrogen gas is not produced at all—or at least not in the form of bubbles. For this reason, those theories which ascribe overpotential to the sluggishness of some stage in the electrodic reaction appear, to the present author, to be unsatisfactory.[1]

As a matter of fact, it is easy to find an analogy for the phenomenon of overpotential.[2] All our experience regarding the evolution of gas in bubbles goes to show that bubbles are never produced until there is considerable supersaturation or superheating. A simple example is afforded by the boiling of water. At 100° C. the vapour pressure of water is equal to that of the atmosphere, and above 100° it exceeds that of the atmosphere; nevertheless it is possible to heat air-free water in a vessel with smooth, clean sides as high as 106° before the formation of bubbles occurs; when boiling does occur, just above 106°, it is of the violent character known as "bumping." If the water contains dissolved air, small air-bubbles are produced on heating the liquid and these form nuclei for the formation of steam-bubbles; in such a case, there is little or no super-heating, ebullition occurring quite smoothly at about 100°. Any roughness on the sides of the vessel likewise aids the formation of steam-bubbles, and serves to prevent super-heating.

Super-heating is very generally regarded as a surface-tension phenomenon. Very minute bubbles possess a very large surface compared to their volume, and, since their content of surface energy is very great, they constitute an unstable form of matter. Now all bubbles are necessarily minute at the moment of their formation, before they have had time to grow to greater size, and this fact prevents the inception of bubbles when the vapour pressure of the liquid only slightly exceeds that of the atmosphere. If, however, the temperature is raised to 106°, the vapour pressure so much exceeds that of the atmosphere that even these minute and unstable bubbles can be formed, and when once a nucleus-bubble has been produced, it grows with an almost explosive velocity, and "bumping" is the result.

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[1] The theory of C. W. Bennett and J. G. Thompson, *J. Phys. Chem.* **20** (1916), 296, although of great interest and no doubt containing an element of truth, cannot scarcely be accepted as a whole. There is likewise difficulty in accepting the theory of N. Isgarischew and S. Berkmann, *Zeitsch. Elektrochem.* **28** (1922), 40, 47.

[2] U. R. Evans, *Trans. Faraday Soc.* **9** (1913), 310; also *Trans. Faraday Soc.* **18** (1922), 10.

The phenomenon of overpotential can be interpreted qualitatively in rather the same way as "bumping." Suppose that an electrolytic cell is fitted with a zinc cathode and is filled with acid, and that a gradually increasing E.M.F. is applied to it. When the cathodic potential reaches 0·0 volts, the surface of the zinc must be regarded as saturated with hydrogen. When it reaches −0·1 volts, it must be supersaturated; but no bubbles of hydrogen are formed. A very little hydrogen may be removed by diffusion through the zinc or by combination with dissolved oxygen, and consequently a certain very small "leakage-current" may pass continuously, which represents the replacement of this removed hydrogen. But no current of any appreciable strength passes until a cathodic potential of −0·70 volt is reached. At that point the supersaturation of the zinc becomes so great that bubble-formation becomes possible, and, hydrogen gas being evolved freely, the current passing becomes quite considerable.

The surface tension theory [1] explains readily the fact that rough surfaces have a smaller overpotential than smooth ones; any irregularity in the surface is favourable for the formationof bubbles. There appears to be a general connection between the overpotential and the "angle of contact" made by the larger bubbles of hydrogen as they cling to the metal of the electrode, an angle which also bears a relation to the surface tension. Qualitatively, therefore, the "surface tension theory" of overpotential seems to explain the facts.

When we attempt to study the matter quantitatively, however, difficulties arise. It is possible roughly to calculate the degree of supersaturation which corresponds to the different overpotentials observed. Amalgamated zinc, for instance, has an overpotential of 0·88 volt; and, according to the simplest method of calculating, this should correspond to a hydrogen pressure of 10^{30} atmospheres.[2] Apparently, it would require a gaseous pressure of 10^{30} atmospheres to saturate the electrode with the gas to the same extent as occurs every time an amalgamated zinc cathode is used in the electrolysis of an acid solution. The method of calculation employed is certainly not exact, but undoubtedly the degree of supersaturation must be very great—if hydrogen is thought to exist in the electrode simply as a dissolved gas. A good deal of thought has been devoted to accounting for the existence of a system involving such a high supersaturation. Newbery prefers to think that the hydrogen exists in the cathode as an unstable metallic hydride ; the fact that the value of the overpotential of a metal seems to have a connection with the valency lends this view some support. It is possible that he is right in thinking that some sort of combination between hydrogen and the cathode metal does occur, but it is doubtful whether hydrides of definite formulæ are ever produced. In any case, such compounds would appear to be rather the effect of overpotential than the cause.

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[1] H. G. Moeller, *Zeitsch. Phys. Chem.* **65** (1909), 226. The view receives considerable support from the important work of D. A. MacInnes and L. Adler, *J. Amer. Chem. Soc.* **41** (1919), 194.

[2] E. Newbery, *Trans. Chem. Soc.* **109** (1916), 1359.

It is, however, probable that the hydrogen which determines the potential of a polarized cathode exists—not dissolved *in* the metal—but adsorbed *upon* the metal, as a film only one atom, or perhaps one molecule, thick. The total amount of this electrically active hydrogen existing upon the cathode is probably very minute, and the ordinary ideas of supersaturation therefore scarcely apply to such a case.[1] The present writer has put forward the suggestion that the hydrogen adsorbed at the cathode surface is in a state intermediate between the atomic and ionic conditions.[2]

Oxygen Overpotential. Overpotential also occurs at an anode in cases of electrolysis where the evolution of oxygen gas is aimed at. It is rather difficult to determine directly the potential at which oxygen ought to be evolved if overpotential did not occur. But the equilibrium potential of the electrode,

Metal saturated with oxygen at 1 atmosphere pressure	Acid of normal hydrion concentration

has been proved, by an indirect method, to be + 1·23 volts.[3]

Under ordinary circumstances, it is always necessary to apply a higher potential than + 1·23 volts before oxygen evolution in bubbles occurs, the excess potential (or overpotential) being shown in the table below.[4] It will be noticed that only the noble metals can be used as anodes in an acid solution under circumstances which give rise to oxygen evolution; other metals would tend to dissolve anodically, and consequently no numbers can be given for the oxygen overpotential upon these materials. In an alkaline solution, some of the more reactive metals can be used as insoluble anodes, and the overpotential of such metals can thus be determined.

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[1] Another view of overpotential, also based upon the idea of an adsorbed film, is given by E. K. Rideal, *J. Amer. Chem. Soc.* **42** (1920), 94. See also H. V. S. Knibbs, *Trans. Faraday Soc.* **18** (1922), 14.

[2] U. R. Evans, *Trans. Faraday Soc.* **18** (1922), 10.

[3] W. Nernst, *Zeitsch. Elektrochem.* **11** (1905), 835. Compare G. N. Lewis, *Zeitsch. Phys. Chem.* **55** (1906), 465, and also J. N. Brönsted, *Zeitsch. Phys. Chem.* **65** (1909), 84.

[4] Values in acid solution quoted from W. A. Caspari, *Zeitsch. Phys. Chem.* **30** (1899), 89. Values in alkaline solution, obtained from results by A. Coehn and Y. Osaka, *Zeitsch. Anorg. Chem.* **34** (1903), 86.

		Alkaline Solution.	Acid Solution.
Nickel, spongy		0·05	
Nickel, smooth		0·12	
Cobalt		0·13	
Iron		0·24	
Platinum, black		0·24	0·39
Platinum, smooth		0·44	0·62
Copper	these metals are visibly oxidized before oxygen is evolved	0·25	
Lead		0·30	
Silver		0·40	
Cadmium		0·42	
Palladium		0·42	0·39
Gold		0·52	0·59

It should be pointed out, however, that there is strong evidence for thinking that some sort of oxide-film is generally formed upon the anode before oxygen evolution takes place; in some cases, lead for instance, the formation of the oxide-film is obvious to the eye, but in other cases, e.g. platinum, the surface of the anode undergoes no visible alteration. The numbers obtained for the overpotential vary very much according to the method used for determining it, and alter with the conditions under which the investigation is carried out.

Overpotential has also been noticed in the anodic evolution of chlorine gas by the electrolysis of the solution of a chloride.[1]

Action of Depolarizers. If to the solution surrounding the anode of a cell a reducing agent is added, which is able to react with—and remove—the oxygen accumulating there without the production of bubbles, we can conduct the electrolysis at a lower anodic potential than is needed where oxygen has to be evolved in gaseous form. Similarly, if the cathode is surrounded by an oxidizing agent, we are enabled to pass current through the cell at a less negative cathodic potential, because the hydrogen is continuously removed in a form which does not involve the formation of gas. Indeed—if the oxidizer is a vigorous one—the hydrogen concentration in the electrode may be kept permanently below the saturation value, and, in that case, current can pass continuously at a potential which is on the positive side of 0·000 volts.

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[1] In addition, the type of polarization which occurs when nickel is deposited from an aqueous solution has, apparently, more in common with the overpotential of gas evolution than with the normal polarization such as attends copper deposition. It seems that deposition will not take place within 0·1 volt of the equilibrium P.D. even at very low current density. The matter requires further investigation. See E. P. Schoch, *Amer. Chem. J.*, **41 (1909), 209.**

Even dissolved oxygen acts in this way. The electrolytic decomposition of acidulated water into oxygen and hydrogen should theoretically be possible at any E.M.F. exceeding 1·23 volts; this theoretical E.M.F. is made up of the difference between the equilibrium value at the two electrodes. Thus:—

P.D. of the electrode H_2 | $H^{\cdot}$ . . .	0·0 volts
P.D. of the electrode O_2 | $H^{\cdot}$ . . .	+ 1·23 volts
Difference =	1·23 volts

In practice, using platinum electrodes and air-free water, owing to the overpotential at both poles, we have to apply a much higher E.M.F., 1·6 to 1·8 volts, before much current begins to pass. But, if we employ water containing dissolved oxygen and use a large cathode, so as to give plenty of scope for the removal of hydrogen, a very appreciable current can be passed through the cell by means of a much lower E.M.F.—about 1 volt.[1] The dissolved oxygen is said to act as a **"depolarizer."**

Use of Depolarizers in Primary Cells. Probably the most interesting examples of oxidizing depolarizers are provided by the various forms of primary cell, and it is highly instructive to trace very briefly the evolution of practical current-producing batteries. The original cell invented by Volta in the year 1800 consisted of two plates of zinc and copper immersed in dilute acid; in this simple couple, the zinc passes into the ionic state at the negative pole, according to the reaction

$$Zn = Zn^{\cdot\cdot} + 2e,$$

whilst on the copper (positive) pole, hydrogen passes from the ionic to the atomic condition

$$2H^{\cdot} + 2e = 2H.$$

When first the plates are immersed in the acid, the E.M.F. produced often exceeds one volt, but as the hydrogen begins to accumulate on the copper pole, the potential at that pole—which is at first positive—becomes zero and finally negative; when hydrogen begins to be evolved in bubbles, the E.M.F. of the combination has usually sunk to about half a volt.

A distinct improvement, due to Smee, was the substitution of a platinized silver plate for the copper plate as the positive pole;

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[1] C. N. Hitchcock, *Trans. Amer. Electrochem. Soc.* **25** (1914), 415.

the rough surface facilitates the liberation of hydrogen in bubbles, and, by reducing the overpotential of hydrogen-generation, increases the working E.M.F. of the cell.

Even in such an arrangement, hydrogen can never be evolved until the positive pole is saturated with the gas. If, however, an oxidizing agent is added to the liquid, the hydrogen can be removed as it is formed, and the concentration of hydrogen at the positive pole can be kept extremely low ; the E.M.F. of the cell is accordingly increased. In the **dichromate cell,** for instance, potassium dichromate or chromic acid is added as an oxidizing depolarizer, and carbon, which is unattacked by these reagents, is used as the positive pole. The arrangement produced,

Zinc	Sulphuric acid and Chromic acid (H_2CrO_4)	Carbon

yields an E.M.F. of about 2·1 volts. It will be remembered that in the last chapter attention was called to the high (positive) P.D. produced when an unattackable electrode, like platinum, was surrounded by a strong oxidizing agent like potassium dichromate.

In nearly all forms of practical primary cells, zinc is used as the negative (attackable) element, and carbon as the positive (unattackable) pole. The cells differ from one another mainly in the choice of the oxidizing depolarizer. Dichromates and chromic acid have the advantage that—when the cell is working—they do not act on the zinc chemically to any great extent, although, as soon as the current is shut off, it is well to raise the zinc pole out of the solution. In the **Bunsen Cell,** however, nitric acid is the depolarizer, and, if this acid were to come into direct contact with the zinc, it would attack that metal ; therefore, a porous partition must be used to shut off the nitric acid surrounding the positive carbon pole from the zinc. The cell consists of the combination,

Zinc	Dilute H_2SO_4	Dilute HNO_3	Carbon

and yields about 1·9 volts.

Of greater practical value, are the cells in which a solid depolarizer is used. In the **Leclanché cell,** the carbon positive rod has a mixture of granular carbon and manganese dioxide rammed tightly round it, the whole mass being contained in a porous pot. Outside this comes a solution of ammonium chloride, containing the negative pole which consists of a stick of zinc. The combination can be written

$$\text{Zinc} \;\Big|\; \begin{matrix} NH_4Cl \\ \text{solution} \end{matrix} \;\Big|\; MnO_2 \;\Big|\; \text{Carbon}$$

The E.M.F. produced by the cell is about 1·5 volts when fresh.

Practically speaking the whole of the granular mass functions as the positive electrode, and it has thus a large active surface. Nevertheless, solid depolarizers, such as manganese dioxide, invariably act more slowly than dissolved ones; and, if the Leclanché cell is called upon to produce a high current for any length of time, hydrogen begins to accumulate at the positive pole, and the E.M.F. drops below a volt; the cell is then said to be "polarized." If, however, it is allowed to stand idle, the hydrogen is gradually removed by the manganese dioxide, and the E.M.F. rises once more.

The so-called "**dry cell,**" which is merely a Leclanché cell adapted for transport without danger of "spilling," is described in the section on manganese (Vol. II).

Another useful cell with a solid depolarizer is the **Lalande.**[1] This consists of the combination

$$\text{Zinc} \;\Big|\; \begin{matrix} NaOH \\ \text{solution} \end{matrix} \;\Big|\; CuO \;\Big|\; \text{Copper}$$

The cupric oxide (CuO) reacts with the hydrogen formed at the positive pole, becoming converted to cuprous oxide (Cu_2O) and even to metallic copper. The cell yields about a volt when fresh, but, as the cupric oxide becomes reduced, it falls considerably.

Efficiency of an Electrolytic Process. The Current Efficiency of an electrolytic process has already been referred to. Faraday's Law states that 96,580 coulombs of electricity (about 26·8 ampere-hours) will be sufficient to deposit at a cathode the equivalent weight of any substance expressed in grams. But it is possible that more than one substance may be produced at the cathode. For instance, in the deposition of nickel from a solution of nickel chloride containing acid, only part of the current may be employed in depositing nickel, much being concerned with the evolution of hydrogen; this evolution causes necessarily a lowering of current efficiency.

Another important cause of low current efficiency is introduced if a salt of a metal like iron, which has two ions $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$, is present in the cell, in which deposition is going on. In this case, much of the current at the cathode is taken up in reducing the ferric ion to the ferrous ion according to the equation

$$Fe^{\cdot\cdot\cdot} + e = Fe^{\cdot\cdot}$$

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[1] See A. J. Allmand, "Principles of Applied Electrochemistry" (Arnold), 1912 edition, pp. 203–206.

If afterwards the ferrous ion is carried by the stirring of the bath to the anodic surface it again becomes oxidized to the ferric ion

$$\mathrm{Fe^{\cdot\cdot}} = \mathrm{Fe^{\cdot\cdot\cdot}} + e$$

and can then return to the cathode, and once more be reduced. It is evident, therefore, that a small amount of iron salt may continue to act as a waster of current for an indefinite time. The only method of preventing this from happening is to divide the cell by means of a porous partition, and thus prevent ferrous ions from travelling from cathode to anode.

If, at any time during electrolysis—or after the current has been shut off—the nickel deposited is chemically attacked by the acid in the bath, or by the oxidizing agents present, the yield of metal obtained is clearly reduced; this constitutes another reason for the diminution of the current efficiency of the process as a whole.

When, therefore, at the end of the operation, we weigh the deposit and express the weight of nickel actually obtained as a percentage of that which would be expected from Faraday's Law—on the assumption that all the current has been devoted to the deposition of nickel—the current efficiency of the process is obtained. The current efficiency of technical electrolytic processes is usually fairly high; it commonly exceeds 70 per cent., and sometimes the manufacturer obtains as much as 95–98 per cent. of the estimated yield.

On the other hand, it is generally necessary to apply to the cell an E.M.F. considerably in excess of the theoretical decomposition voltage if the process is to be carried on at a reasonable speed. A considerable P.D. must be made to fall over the liquid within the cell to obtain the necessary movement of ions towards the electrodes; in addition, at each electrode, polarization occurs, which increases as the current density is raised; and where a gas is to be evolved at an electrode, overpotential has to be provided for.

If the theoretical decomposition voltage is expressed as a fraction of the working E.M.F. employed, the fraction is a measure of the **E.M.F. efficiency of the process.** For instance, if the theoretical decomposition voltage is 2·2 volts and the working E.M.F. applied to the cell is 3·3 volts, the fraction is $\frac{2 \cdot 2}{3 \cdot 3} = 0 \cdot 67$.

The energy efficiency denotes the theoretical energy required to bring about a change electrolytically expressed as a percentage of the energy actually consumed under working conditions. Since

electrical energy = quantity of electricity × P.D.

the energy efficiency is obtained by multiplying the current efficiency by the fraction representing the E.M.F. efficiency. Thus if the current efficiency of a process is 90 per cent., and the E.M.F. efficiency is 0·67, the energy efficiency is

$$0{\cdot}67 \times 90 \text{ per cent.} = 60 \text{ per cent.}$$

Efficiency of a Current-Producing Cell. The conceptions of current efficiency, E.M.F. efficiency and energy efficiency can equally well be applied to a current-producing cell. Faraday's Law holds good here also, and consequently 32·68 grams of zinc should produce 96,580 coulombs (or 26·8 ampere-hours) in whatever form of cell it is consumed, assuming always that the zinc is only dissolved in such a way as to generate current. If, however, in a cell, the zinc suffers local corrosion, of a kind that generates no current outside the cell, we shall not obtain the complete 96,580 coulombs of electricity. By expressing the quantity actually obtained as a percentage of that theoretically possible, we have the current efficiency of the cell.

Each cell has a certain maximum E.M.F. (1·096 volts in the case of the Daniell cell). If—owing to polarization or to the fact that part of the total P.D. falls within the cell itself—it actually yields a lower P.D. over the external circuit, we can regard the fraction

$$\frac{\text{E.M.F. actually obtained}}{\text{maximum E.M.F. possible}}$$

as the E.M.F. efficiency of the cell. The product of current efficiency and E.M.F. efficiency gives the energy efficiency. The energy efficiency of primary cells in common use is usually high, sometimes 90 per cent.

Summary. The equilibrium value of the potential at an electrode surface alters when a current passes, becoming lower (more negative) at a cathode and higher (more positive) at an anode; this departure from the equilibrium value is called **polarization.** Thus although an E.M.F. just exceeding the equilibrium value will send a slight current through an electrolytic cell, the equilibrium value must be exceeded by a considerable amount if a large current is to be forced through. A current-producing cell likewise shows polarization, the total E.M.F. yielded by the combination dropping off whenever it is required to generate a high current. Polarization is due partly to the naturally limited velocity of electrodic reactions, partly to concentration changes at the electrode surfaces (due to the limited velocity of diffusion), and partly to the accumulation of products of reaction (e.g. gases) in or on the electrodes.

Whilst the polarization attending the deposition of *metals* can usually be rendered negligibly small by working very slowly, i.e. at a very small current density, the evolution of *gases* does not commence at all until the equilibrium potential is passed by a definite amount, called the **overpotential.** The overpotential depends on the nature of the electrode material and also on the character of the surface, being smaller for a rough surface than a smooth one. It is closely connected with surface tension, and is probably due to the abnormally high surface energy of minute gas bubbles; every bubble is minute at the moment of its formation.

An oxidizing agent at a cathode, or a reducing agent at an anode, usually acts as a "**depolarizer,**" destroying the products of decomposition before they are able to accumulate, and thus rendering the potential needed for the passage of current less negative in the first case, and less positive in the second. The critical decomposition E.M.F. of acidulated water is 1·23 volts, but a current will pass between electrodes immersed in acidulated water containing dissolved oxygen at a much lower voltage.

In current-producing cells, oxidizing agents (dichromates, nitric acid or manganese dioxide) are employed as depolarizers to keep the hydrogen-concentration at the positive pole as low as possible. Cells containing depolarizers necessarily give higher E.M.F.s than the old type of cell in which gaseous hydrogen was produced, even though in the older type overpotential might be practically overcome (as in the Smee cell) by the employment of a positive pole with roughened surface.

The current efficiency of a process of electro-deposition is the yield of metal obtained at the cathode expressed as a percentage of the yield calculated by Faraday's Law. It drops below 100 per cent. if hydrogen is evolved, or if an oxidizing agent (e.g. a ferric salt) is present in solution which will be reduced cathodically (thus wasting current), or which, alternatively, may redissolve the deposited metal (thus reducing the yield).

The E.M.F. efficiency is the theoretical E.M.F. needed for the decomposition expressed as a fraction of the E.M.F. actually employed. It is reduced both by polarization and by overpotential The energy efficiency is the product of the current efficiency and E.M.F. efficiency.

CHAPTER XI

THE DEPOSITION OF METAL UPON THE CATHODE

General. There are numerous occasions on which it is desirable to deposit a metal electrolytically from a solution of a salt. It will facilitate the understanding of the present chapter, if a few of the more important cases are mentioned.

(1) In the **electrolytic reduction** of a metal from the ore, the ore (roasted, if necessary) is leached with an acid (or other reagent) so as to give a solution of a salt of the metal in question. This solution is then electrolysed, in a cell fitted with an insoluble anode; the metal is deposited on the cathode, and the acid is regenerated as a result of the anodic reaction, and can be used to leach more ore. When the cathodic deposit becomes inconveniently thick, it is removed and melted down in a furnace. In this case, therefore, so long as the deposit is sufficiently coherent to hold together until it reaches the furnace, the physical character is not of great importance.

(2) In the **electro-refining** of a metal, soluble anodes consisting of the impure metal to be refined are immersed in a bath containing a salt of the metal; the cathodes usually consist of thin sheets of pure metal. Under ideal conditions, *pure* metal is deposited on the cathodes and a nearly equal amount is dissolved at the anodes. The impurities either remain undissolved as an "anode sludge," or, if dissolved, are not co-deposited on the cathodes. Here again, the cathode deposit is generally remelted before use, in which case only a moderately coherent form of metal is needed. However, attempts have been made at different times to deposit the pure metal in the form in which it will finally be used, thus avoiding the process of remelting; if such an attempt is to succeed, an extremely non-porous, compact deposit is called for.

(3) In **electro-plating**, a very thin but extremely *smooth* and coherent film of metal has to be deposited upon an article of another metal, which is made the cathode. A soluble anode consisting of the metal to be deposited is generally employed, so as to keep

the bath replenished. In electro-plating the extreme smoothness of the deposit is essential, so that it will take a high polish; it must be non-porous and strongly adherent.

(4) In **electro-analysis,** the *complete* deposition of a quantity of metal from a salt solution upon a cathode, weighed before the process, is required, an insoluble anode being invariably employed. Here the deposit must be sufficiently coherent and adherent to allow of rapid drying without oxidation and accurate weighing; it must contain the whole of the metal in the solution, but nothing else besides.

Now, although all these processes are essentially different, the changes occurring at the cathode are governed in each case by the same principles, and are not directly affected by what may be proceeding at the anode, although they may be affected indirectly if the anodic reaction introduces a change in the composition of the solution. It is possible to study cathodic changes in a general manner without reference to the accompanying anodic changes, and the present chapter will be devoted to the study of "cathodic deposition." The succeeding chapter, on the other hand, will be devoted to "anodic dissolution," considered quite independently of the accompanying cathodic change.

Current Efficiency in the Deposition of Different Metals. Let us first consider the electrolysis of a salt of a comparatively "noble" metal, a metal which stands well above hydrogen in the Potential Series—copper, silver or gold, for instance. In such a case, the decomposition voltage is low; the application of a comparatively small E.M.F. will serve to reduce the potential at the cathode below the electrode potential of the metal in question, and discharge of the ions will commence, causing a deposit of the metal to form upon the cathode. Since there is, as a rule, no other reaction that can occur at the cathode, the current efficiency is usually extremely high.

But now consider the deposition of a salt of nickel, a metal which stands below hydrogen in the Potential Series. Here it is necessary to apply an E.M.F. sufficient to depress the cathodic potential below −0·2 volts, before the deposition is theoretically possible; actually, in order to obtain deposition at any appreciable speed, it must be depressed much lower, say to −0·5 volts.[1] At such a value, however, there is a great likelihood that hydrogen evolution may also occur. If the nickel salt solution contains a strong acid, the cathode becomes saturated with hydrogen at about 0·00 volts, and although, owing to overpotential, the evolution of gas may not occur until the cathode potential reaches about $-0{\cdot}21$ volts, it will be taking place freely at, say, $-0{\cdot}5$ volts. Hence the deposition of nickel from a strongly acid solution is always a very inefficient operation; much of the current which passes is used for the evolution of hydrogen, and not for the production of metallic nickel.

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[1] See E. P. Schoch, *Amer. Chem. J.* **41** (1909), 221–227; especially curves on page 225. It should be noted that the values of the potentials referred to by Schoch are expressed on the so-called "absolute" scale.

If the nickel salt solution is neutral, the hydrogen evolution is largely prevented. The equilibrium potential

$$H_2 \mid \text{Neutral solution}$$

is $-0{\cdot}406$ volts, and, owing to overpotential, hydrogen is unlikely to be evolved until the cathodic potential is depressed to about $-0{\cdot}6$ volts, a value more negative than that required for the deposition of nickel; the current efficiency is therefore much greater when we use a neutral bath.[1] However, as will be explained later on, a neutral bath usually gives an incoherent deposit of metal, owing to the co-deposition of hydroxides. If a good deposit is aimed at, a feeble acid—such as boric or acetic acid—which yields a low hydrion concentration—is employed. Although this actually allows the production of a certain amount of hydrogen, the current efficiency of the process is usually fairly high (70–80 per cent.).

As we pass down the Potential Series, the efficient deposition of metals becomes—on the whole—more and more difficult. There is a remarkable exception, however, in the case of zinc which can be deposited at nearly 100 per cent. efficiency from pure solutions, even when they contain a small concentration of a weak acid. This fact is due to the remarkably high value for the overpotential of hydrogen-evolution upon a smooth zinc surface. So long as the zinc deposit remains smooth and free from impurities, hydrogen-evolution does not take place at the potential needed for the slow deposition of zinc; but, should the surface become rough or spongy, or should traces of metals of low overpotential (such as copper or iron) get into the bath, and be deposited along with the zinc, hydrogen-evolution at once starts and the current efficiency drops; or again, if the current density is made too high, causing the cathodic potential to sink much below $-0{\cdot}770$ volts, vigorous hydrogen-evolution will occur, and the current efficiency will be low.

Some of the other metals in this part of the Potential Series are very difficult to deposit from aqueous solution. The efficient deposition of manganese,[1] for instance, requires careful control of the current density; the current efficiency is greatly reduced on adding a small amount of acid to the solution, and, if large amounts are added, it sinks to zero. The deposition from aqueous solution of the metals below manganese—aluminium, magnesium, sodium, potassium and the others—is practically impossible. The electrolysis of a solution of sodium chloride, for instance, only gives rise to hydrogen at the cathode, around which the solution—if neutral at the start—soon becomes alkaline. Nor is the absence of a metallic deposit remarkable; even if a film of sodium were momentarily formed, it would at once react with water producing hydrogen and sodium hydroxide. When, however, a cathode consisting of mercury is used in the electrolysis of a sodium chloride solution, an amalgam—that is, a solution of sodium in mercury—is produced. The formation of the amalgam is possible, partly because a less negative potential is required for the formation of dilute sodium amalgam than for the formation of pure sodium, and partly because the high overpotential of mercury is unfavourable to the evolution of hydrogen gas.

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[1] E. F. Kern and F. G. Fabian, *Electrochem. Ind.* **6** (1908), 365. See also L. H. Hammond, *Trans. Amer. Electrochem. Soc.* **30** (1916), 127; R. Riedel, *Zeitsch. Elektrochem.* **21** (1915), 5.

A large number of metals occurring in Groups IVA, VA and VIA of the Periodic Table are also incapable of being deposited electrolytically from the aqueous solutions of their salts, but here the reason is somewhat different. The metals of these groups do not occur in aqueous solution, to any great extent, as cations; the principle oxides of vanadium, tantalum, molybdenum and tungsten have an acidic character and the metal exists in the anion; even where lower oxides of a basic character are known, the metal generally exists rather as a complex cation, such as $[VO]^{\cdot\cdot}$ than as a simple cation $V^{\cdot\cdot\cdot\cdot}$; similar complex cations, such as $[ZrO]^{\cdot\cdot}$, appear to exist in metals of Group IVA. It is not surprising to find that the electrolysis of such solutions produces nothing except lower oxides and hydroxides upon the cathode.

The normal electrode potentials of most of these metals are not known with any certainty (most of the determinations given in electrochemical literature are based upon assumptions, which, in the opinion of the present writer, are unjustified). But it is very likely that many of these metals stand on the "noble" side of zinc in the Potential Series, and that the practical difficulty in carrying out the electrolytic deposition is due only to the difficulty in finding a solution which will contain anything approaching normal—or, indeed, even milli-normal—concentration of metallic ions.

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[1] G. D. von Arsdale and C. G. Maier, *Trans. Amer. Electrochem. Soc.* **33** (1918), 109.

Co-deposition of Oxides or Hydroxides. Spongy or Incoherent Deposits. It has been stated above that metal deposited from a neutral solution is usually of an incoherent spongy character. The reason for this can be explained at once. If from a neutral solution, any generation of hydrogen occurs, the withdrawal of the hydrion at the cathode necessarily leaves an excess of hydroxyl at the boundary of the cathode itself; in other words, there is an alkaline film along the surface of the electrode. As a result, hydroxide (or perhaps oxide) is liable to be precipitated at this point, and the precipitate will get caught between the growing crystals of the metal; the deposit will not consist of metal alone, but metal mixed with hydroxide, and this will probably be obvious to the observer by the dark colour, dull appearance, and loose incoherent spongy character.

It has long been known that the formation of a "spongy" deposit often follows hard upon the evolution of hydrogen, and early observers often attributed the sponginess to the disintegrating action of the hydrogen bubbles. Actually the gas-evolution—as such—may help to make the deposition uneven, but the main cause of sponginess is certainly the slight alkalinity which is a necessary consequence of hydrogen-production in a previously neutral solution.[1]

In fact, by varying the conditions under which the electrolysis of a solution of a salt of iron, nickel, cobalt, zinc, cadmium or manganese is carried out, it is possible to obtain—at will—either the deposition of the metal, or the deposition of the hydroxide.[2] If the solution is concentrated and distinctly acid, the metal is deposited; if the solution is dilute and neutral, the deposit consists mainly of hydroxide.

The reason why a dilute solution is favourable to the formation of hydroxide is very simple. If the supply of metallic ions at the cathode surface becomes exhausted, only one reaction can occur there, namely, the evolution of hydrogen; the solution thus becomes alkaline and precipitation of hydroxide follows. Evidently, the more concentrated the solution, the less likely is the layer next to the cathode to become exhausted of metallic ions.

Clearly the rate of deposition—that is to say, the current density—will have an important influence in determining whether exhaustion of metallic ions can occur or not. An unduly high current density will often lead to spongy deposits. If, however, the solution is vigorously stirred during deposition, the exhaustion round the cathode can be prevented even at quite high current densities. Therefore, from an agitated solution, deposition can be conducted—without fear of sponginess—at a much higher current density than in an unstirred bath.

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[1] W. D. Bancroft, *J. Phys. Chem.* 9 (1905), 277.

[2] J. H. Paterson, *Proc. Univ. Durham Phil. Soc.* 4 (1912), 187; abstract, *J. Chem. Soc.* 104 (1913), ii. 100.

The matter can be summarized in a few words. If a coherent deposit of metal—free from sponginess—is desired, the concentration of metallic salt should be kept high, the solution should be kept well stirred, the current density should not be excessive, and the solution should be kept distinctly acid.

If the use of an acid solution is not desired on account of the danger of low current efficiency, some other addition may be made which will avert the danger of co-deposition of hydroxides. If the metal has a distinctly amphoteric character—as in the case of tin—a good deposit can often be obtained from a distinctly alkaline bath. In such instance, it is only the neutral solutions which are objectionable; baths distinctly acid or distinctly alkaline usually give deposits free from sponginess. Many of the other additions which are commonly made to deposition baths—tartrates, oxalates, ammonia and ammonium salts—are substances which act as solvents for oxide. One reason—although not the only reason—why clean deposits are usually obtained from baths containing potassium cyanide is that any hydroxide deposited would at once be dissolved by the cyanide solution.

On the other hand, the salts of weak organic acids—such as acetates—are to be avoided in the production of an electrolytic deposit; for such salts favour hydrolysis and the consequent co-precipitation of hydroxide.

The effect of the temperature of the bath upon the character of the deposit is twofold. In the first place, a high temperature increases the rate of diffusion, and therefore is likely to diminish the danger of exhaustion near the cathode; from this point of view, a high temperature is favourable to the coherence of the deposit. On the other hand, the overpotential of hydrogen evolution greatly diminishes as the temperature rises, and in many cases deposition from a warm bath involves an undue evolution of hydrogen. This second effect is often the most important and a rise of temperature is, on the whole, unfavourable to the character of the deposit. Metals like zinc, the successful deposition of which depends entirely on the high overpotential of hydrogen, should always be deposited from a cool bath.

Conditions for compact Deposits. We have just considered the conditions which must be observed if the co-deposition of hydroxide—with consequent sponginess of the metal—is to be avoided. But even if these conditions are successfully maintained, the metallic deposit, though quite free from hydroxide or other weakening impurities, may nevertheless often have an incoherent character. It is necessary, therefore, to consider the way in which the atoms of metal array themselves upon the cathode.

The crystallization of copper from a normal copper sulphate solution upon an electrode the potential of which is depressed below + 0·329 volts (the equilibrium value) is really very closely analogous to the crystallization from molten copper at the sides of a steel mould, the temperature of which is kept below the melting-point of copper ; as a matter of fact the structure produced in the two cases has many features in common. At the electrode surface, crystallization commences at certain points and the minute crystals produced act as nuclei for further growth ; there is only one direction in which the crystallites starting from the various nuclei can grow indefinitely without interfering with one another, and that direction is perpendicular to the electrode. As a result, the structure of the copper deposited consists of long finger-like crystallites perpendicular to the electrode surface.[1] The number of nuclei formed will depend largely on the extent to which the potential departs from the equilibrium value. At low current density—which involves only a small departure from the equilibrium potential—comparatively few nuclei are produced, whilst, at high current density, where the potential is very different from the equilibrium value, the nuclei are crowded close together on the electrode surface.[2] It follows that, at a low current density, the crystallites are comparatively broad, as shown in Fig. 84A, whilst at high current density, the crystallites are narrower and the whole structure is much finer (Fig. 84B). In either case the size of the crystal-grains of the deposit is finer at the original surface of the cathode than further from it, presumably because some of the crystal-nuclei formed when deposition first commences are orientated in such a way that they do not grow quickly in the direction perpendicular to the surface ; the zone of comparatively small crystals next to the original cathode surface is best seen in Fig. 84A.

Yet another circumstance will tend to make the structure of the deposit obtained at high current density finer than that of the deposit produced at low current density ; at high current density, where the departure from equilibrium conditions is considerable, fresh nuclei will be formed continually as deposition occurs and the length of the crystals is limited, whilst at low current density, the same crystals will continue to grow out for a very considerable distance.

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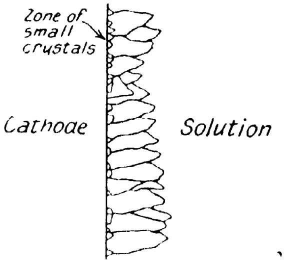
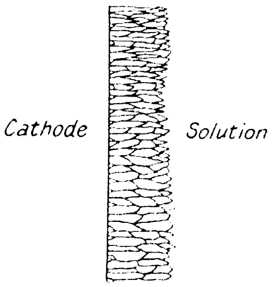
[1] O. Faust, *Zeitsch. Anorg. Chem.* 78 (1912), 201 ; W. Blum, H. D. Holler, and H. S. Rawdon, *Trans. Amer. Electrochem. Soc.* 30 (1916), 159 ; M. von Schwartz, *Int. Zeitsch. Met.* 7 (1915), 124.

[2] Compare, especially, A. H. W. Aten and L. M. Boerlage, *Rec. Trav. Chim.* 39 (1920), 720.

Very important is the effect of current density upon the compactness and smoothness of the deposit; the coarse crystals obtained at low current density are not always in close contact with one another, and tend to fall apart when the deposit is handled; the surface is irregular and the deposit itself distinctly porous. On the other hand, in metals obtained at high current density, the different crystals adhere strongly one to the other; the deposit is compact and usually non-porous; the surface is smooth, so that the crystalline character would not be suspected until a micro-section is examined. Often the micro-sections reveal twin crystals, an indication of lateral pressure exerted by the growing crystallites on one another. And, whilst the structure of the deposit obtained at low current density scarcely changes on annealing, that obtained at high current density undergoes complete recrystallization when annealed. This is yet another sign that the crystals of the fine-grained deposit press heavily against one another, since recrystallization on annealing rarely occurs unless the metal is in a state of stress.



(A) Low Current Density.



(B) Fairly High Current Density.

FIG. 84.—Electrolytic Deposits Produced at (A) Low Current Density, (B) Fairly High Current Density.

The porosity of the slowly produced deposit is easy to understand; deposition only occurs at the most favourable points, namely at the tips of the finger-like crystals; in the "troughs" between them, which are further from the anode, deposition may perhaps not occur at all, and the different crystals will not "grow into contact." On the other hand, at high current density, provided that the stirring is sufficiently vigorous to ensure a continuous supply of metallic salt in the "troughs," the potential is such that deposition occurs everywhere; the V-shaped terminations of the crystals grow sideways as well as forwards, and good cohesion is obtained between the different grains. But the "proviso" is rather important. As long as the stirring is sufficient, any increase of current density makes the deposit finer, smoother and more coherent. But if the stirring is insufficient, there are limitations to the current density that can profitably be employed; beyond a certain limiting current density, any further increase makes the grain coarse again, the surface rough and the deposit non-compact. Undoubtedly, this irregularity of growth is due to local variation of concentration, and the value of the limiting current density can be raised by increasing the concentration of the bath, or, alternatively, by increasing the rate of stirring.[1]

It is evident, therefore, that, in order to obtain a smooth, coherent, non-porous deposit, the current density must be maintained within certain limits; it must not be too high, or the deposit will be irregular, and possibly spongy, owing to the co-deposition of hydroxides; it must not be too low, or the metal will be coarsely crystalline, incoherent and porous. The limits are often narrow, but become less narrow if the bath is kept well stirred, and the concentration of the metallic salt is high.

It is most important that the conditions should be correct throughout the whole process; for, if at any point roughness should set in, it is unlikely that any degree of subsequent care will eliminate it. On the contrary, the roughness will increase. Any excrescences, however small, will constitute more favourable places for deposition than the depressions that lie between them; for firstly, they will receive more rapid replenishment of metallic salts from the body of the solution; secondly, they are nearer to the anode and the current density will be greater than elsewhere. As deposition proceeds, therefore, the excrescences become greater and greater, and cause the phenomenon known as "treeing"; it is, of course, closely connected to the production of dendritic growths in the crystallization from the molten state. Treeing occurs more in soft metals (lead, tin, cadmium, and thallium) than in hard ones.[2]

If only a thin deposit is aimed at, it is not particularly difficult to ensure that it is compact and uniform. But, since any roughness—however small it may be at first—almost invariably increases as deposition continues, the production of thick deposits of a coherent character is less easy. There is a special tendency for "beards" or excrescences to grow at the sharp corners of the electrodes—a tendency which can readily be understood.[1] In the electro-refining of metals, it is usually possible, by observing the conditions outlined above, to obtain a thick deposit sufficiently coherent to hang together until the process is over, after which the deposit is washed and melted down for use. It would of course save much fuel and much labour if the metal could be deposited directly in the form in which it is to be used. Supposing, for instance, copper is being deposited with a view to the manufacture of tubes, it might be thought possible to produce a thick deposit of copper upon the outside of a steel rod, and afterwards to slip the deposit off the rod; in such a way a thin seamless tube of refined copper would be produced without melting or mechanical treatment. It is found, however, that—unless special precautions are taken—copper tubes produced in this way are too porous and incoherent to stand much pressure. Much ingenuity has been brought to bear upon the problem of obtaining a thoroughly compact deposit of copper by an electrolytic process. Methods have been worked out in which the copper deposit is hammered, rolled or burnished continuously, during the electrolytic process, so that any excrescence that occurs at any point is at once flattened out whilst it is very small; in one method the surface is continuously bombarded by small glass balls throughout the deposition. Many of these processes have been used on a large scale, from time to time, in different parts of the world, but it is doubtful whether all the difficulties have been fully overcome.[2]

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[1] A. Sieverts and W. Wippelmann, *Zeitsch. Anorg. Chem.* **91** (1915), 1; W. E. Hughes, *J. Phys. Chem.* **25** (1921), 495, especially p. 502.

[2] A. Betts, *Trans. Amer. Electrochem. Soc.* **8** (1905), 80.

Adhesion of the Deposit. It is necessary to distinguish between the *cohesion* of the various crystals of the deposit, and the *adhesion* of the deposit to the underlying metal forming the cathode, which in general will not be composed of the metal that is being deposited. The question of adhesion is of considerable importance, especially to the electro-plater.

The adhesion of the deposit to the cathode is capable of quantitative investigation. After deposition is finished, a small round copper block can be soldered to the face of the deposit and the force required to tear away the block (and with it the deposited film) from the surface of the metal below, can then be measured experimentally.[1]

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[1] Some interesting descriptions of the excrescences—particularly those on the edge of the cathode—illustrated by good photographs, are given by G. K. Burgess and C. Hambuechen, *Electrochem. Ind.* **1** (1903), 204.

[2] Many of the older processes are described by W. Pfanhauser, "Manufacture of Metallic Articles Electrolytically. Electro-engraving"; translation by J. W. Richards (Chemical Publishing Co.). Chapter XIII. The microstructure of the deposits obtained by this sort of process is described by A. Sieverts and W. Wippelmann, *Zeitsch. Anorg. Chem.* **93** (1915), 287.

It is found that a deposit adheres better to a rough surface than to a smooth one, as is to be expected. It is also found that a deposit adheres better to a soft cathode-metal than to a hard one; nickel adheres to lead better than to steel. Metals which alloy together adhere better than those which do not; evidently in many cases a layer of alloy forms an intermediate zone connecting the two metals together; thus nickel adheres better to copper than to lead.[2]

Absolute cleanliness of the cathode surface is essential if an adherent deposit is to be obtained, and special precautions are taken by electro-platers to remove the film of grease and of oxide which generally exists on all metals.[3] Usually the first cleaning is largely mechanical, the surface being scoured with wire-brushes to remove the scale. The grease is removed by treatment with hot alkaline solution, or occasionally with benzene or petroleum, and the closely-adherent film of oxide by "pickling" in acid. A process of cathodic cleansing has also given good results; the article to be cleansed is made the cathode in a bath containing acid or sodium chloride; the hydrogen bubbles produced on the surface loosen the adherent impurities, and apparently also bring about a chemical reduction of the oxide present.[4] When sodium chloride is used, the layer of alkali which is produced all over the surface of the cathode exerts a powerful influence in dissolving the grease. Anodic cleansing has also been recommended, as a substitute for acid pickling or cathodic cleansing in cases (like the plating of spring steel wire) where the presence of hydrogen would render the metal brittle.[5]

In some metals—notably aluminium—the oxide-film is almost impossible to remove, and the electro-plating of such materials presents great difficulty.[6]

Another cause of the non-adhesion of a deposit is the tension of the deposited film. Nickel—especially if deposited from an acid bath—often shows a tendency to come peeling off in a tight roll. The natural tension in an electrolytically produced nickel film has been demonstrated by depositing nickel on one side of a straight steel ruler; after the plating-process the ruler is found to be distinctly curved, the plated side being concave.[1]

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[1] M. Schlötter, *Chem. Zeit.* 38 (1914), 289.

[2] K. Kahlenberg, *Electrochem. Ind.* 1 (1903), 201.

[3] See G. Langbein, "Complete Treatise on the Electrodeposition of Metals"; translation by N. T. Brannt (Baird). Chapter V. Also W. Pfanhauser, "Die Electrolytischen Metall-niederschlage" (Springer), 1910 edition, pp. 240–282.

[4] M. de K. Thompson and O. L. Mahlman, *Trans. Amer. Electrochem. Soc.* 31 (1917), 181.

[5] J. Coulson, *Trans. Amer. Electrochem. Soc.* 32 (1917), 237.

[6] W. Pfanhauser, "Die Electrolytischen Metall-niederschlage" (Springer), 1910 edition, p. 619. See also the section on Aluminium in Vol. II of this book.

The tension of the deposited film is observed most readily in those metals—such as iron, nickel, and platinum—which dissolve hydrogen.[2] No doubt the deposited metals at the moment of production are supersaturated with the gas and are in a comparatively voluminous form; presumably the excess of hydrogen is afterwards given up and the nickel left behind tends to contract. Iron and nickel adhere better to the cathode if the plating is conducted from a hot solution. It has been shown that the amount of hydrogen taken up by the deposit is smaller at the high temperature.

The presence of hydrogen in electrolytic nickel and iron causes considerable brittleness in them, and this fact is no doubt responsible for the cracking of the deposit which must precede the peeling. The brittleness is only temporary; after the hydrogen is removed by annealing, electrodeposited iron becomes soft and malleable.

A very remarkable case of tension in a deposited metal is that of antimony deposited from a chloride bath containing free acid; the tension is so great that the deposit breaks with a cracking sound, if struck or locally heated. Such a deposit is known as "explosive antimony"; it contains antimony chloride, apparently as an essential constituent, the chloride being liberated when the deposit "explodes."

It has been stated above that, in electro-plating, the adherence of the film is all-important, and that drastic measures are taken to remove the films of grease or oxide from the article to be plated. It is rather interesting to note that, where it is desired ultimately to remove the deposit from the cathode—as, for instance, in the production of copper tubes referred to above—it is necessary, before the electrolysis commences, to produce artificially upon the cathode a film of grease, oxide or sulphide, which prevents the deposit from adhering too strongly, and assists the subsequent removal. In certain cases the cathode is treated with a special wash containing flaky graphite, which facilitates stripping.

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[1] G. G. Stoney, *Proc. Roy. Soc.* **82** [A] (1909), 172. Compare G. Aliverti, *Atti. Accad. Lincei* **29** (1920), 453.

[2] Two slightly different interpretations of the facts are given respectively by R. Riedel, *Zeitsch. Elektrochem.* **22** (1916), 281, and by V. Kohlschütter and E. Vuilleumier, *Zeitsch. Elektrochem.* **24** (1918), 300. See also V. Kohlschütter and H. Schödl, *Helv. Chim. Acta*, **5** (1922), 490.

Deposition from Solutions of Complex Salts. In electroplating a thin deposit of extraordinary smoothness is demanded. In order to obtain the necessary smoothness, the "grain-size" of the deposit must be made far smaller than anything required in ordinary electro-refining. To reduce the grain-size, it is necessary to cause considerable departure from the equilibrium potential. One way to obtain this would be to work at very high current density, but for work at high current densities very rapid stirring is needed; very bright and smooth deposits of copper, of a grain-size so small that they are practically amorphous, can be obtained from a violently agitated sulphate solution when high current densities are employed. In actual practice, however, it is usually inconvenient to stir the solution so violently, and it is preferable to use a bath where high cathodic polarization occurs at quite low current densities.

It has been stated in the last chapter that polarization occurs much more freely in solutions of salts containing the metal as a complex anion than from solutions of normal salts such as sulphates. It is not surprising, therefore, to find that smooth deposits—so very fine as to be apparently structureless—are obtained from baths containing complex salts, even at fairly low current densities, such as do not involve undue agitation. The smoothest deposits of silver are obtained from cyanide solutions, in which the rare metal exists almost entirely in the complex anions. The rapid alteration of the cathodic potential with the current density in such solutions is no doubt—as explained in the last chapter—due to the paucity of silver ions: but, since there is always a certain small concentration of these ions in equilibrium with complex anions,

$$\mathrm{K}^{\cdot} + [\mathrm{AgCN}]' \rightleftharpoons \mathrm{K}^{\cdot} + \mathrm{Ag}^{\cdot} + 2\mathrm{CN}'.$$

complete exhaustion of silver ions at the cathode surface never occurs. As quickly as the silver ions are used up, fresh ones are formed from the complex $[\mathrm{AgCN}]'$. The use of a complex salt is really a device for keeping the ion-concentration low, without running any risk of complete exhaustion.[1]

The deposition of gold is also conducted from cyanide solutions, whilst good deposits of tin are obtained by the use of solutions containing complex oxalates or tartrates. The use of complex oxalates has proved very successful in electro-analysis for the deposition of zinc, nickel, tin, and iron, whilst complex tartrates are employed for the deposition of bismuth.

Although, owing to the fine structure, deposits obtained from cyanide or other complex baths are often loosely referred to as "amorphous," it is fairly certain that they are really of a crystalline character, essentially like that of deposits from other baths, although it may require a high-power microscope to reveal the individual grains.[1]

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[1] See W. D. Bancroft, *J. Phys. Chem.* **12** (1908), 36; W. Blum, *Trans. Amer. Electrochem. Soc.* **36** (1919), 223.

The employment of complex salts in plating became common long before the cause of their action was understood. It is, indeed, quite likely that the well-known merits of cyanide and other complex baths depends partly on other factors in addition to those just discussed. Cyanides, tartrates and oxalates—as was pointed out early in the chapter—are all good solvents for hydroxides, and would therefore tend to prevent co-deposition of hydroxide, which might lead to sponginess. Yet another view of the use of complex salts, and especially of cyanides, is held by many chemists. It is considered that the primary reaction in the electrolysis of the complex cyanide $K[Ag(CN)_2]$ consists in the discharge of the potassium ions

$$K^{\cdot} + e = K.$$

A deposit of metallic potassium cannot, of course, be produced, but it is very likely that a thin layer of an alloy of potassium with the cathode metal may be formed right over the surface of the electrode. The potassium then reacts with the complex salts, thus:—

$$K + KAg(CN)_2 = Ag + 2KCN.$$

Metallic silver is therefore produced by a secondary reaction, and the silver atoms will be formed, presumably, where the potassium ions were discharged a moment before. Such a conception seems to suggest an explanation for the close adherence of the silver to the underlying metal, and for the fine-grained, and apparently amorphous, character of the deposit.[2]

Colloid Addition Agents. It has also been found that the addition of small amounts of certain substances—usually colloids—to the deposition bath often benefits the character of the deposit. The presence of gelatine, for instance, in an acid copper sulphate bath causes the copper deposit to be shiny, compact and less obviously crystalline.

The presence of the colloid appears to have two distinct effects.[3] In the first place, it renders the grain-size smaller. In this respect the addition of colloids is similar to that of substances like cyanides and tartrates, which, owing to the formation of complex ions, tend to reduce the concentration of simple metallic ions. The fact that the addition of colloids, like the addition of cyanides, greatly increases the cathodic polarization, suggests that the explanation based on the formation of complexes, which has been accepted in the case of cyanides, may be extended to the case of colloids.[1] If the gelatine particles in the copper sulphate solution are imagined to adsorb copper ions, forming complexes—an occurrence which, from our knowledge of colloid chemistry, is known to take place in acid solution[2]—the number of free simple copper cations present will be reduced; consequently the polarization corresponding to any given current density will increase, and the grain-size will accordingly diminish.

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[1] W. E. Hughes, *J. Phys. Chem.* **25** (1921), 497.

[2] Compare R. S. Dean and M. Y. Cheng, *Met. Chem. Eng.* **19** (1918), 83.

[3] A. Sieverts and W. Wippelmann, *Zeitsch. Anorg. Chem.* **91** (1915), 32.

The refinement of the grain caused by small additions of colloids is thus analogous to that caused by the addition of cyanides, tartrates or similar salts. The addition of colloids, however, appears to have a second distinct action, since it entirely alters the structure of the deposit. Instead of consisting of thin finger-like crystallites growing at right angles to the cathode surface, copper deposited in the presence of much gelatine or albumin has a scaly, laminated character, the lamination being roughly parallel to the surface of the cathode. The laminations are said[3] to consist of alternate layers of metallic copper and of the colloidal substance. That such a deposit should be more "shiny" than ordinary electrolytic copper is not difficult to understand.

The cause of the lamination is extremely interesting. The fact that the structure of copper deposited from a bath containing gelatine is so essentially different from that obtained from a colloid-free bath makes it natural to suspect that the metal itself is—in the first case—deposited in the colloidal condition. There is no doubt that the gelatine is deposited—in some sense—along with the copper, for the copper deposit weighs more when gelatine is present than when it is absent; if the copper deposit is heated in hydrogen, much of the excess weight disappears. Moreover, if the plating bath is alkaline instead of acid, the addition of gelatine has no effect; in alkaline solution, it will be remembered, the gelatine particles have a negative charge, and migrate towards the anode, not towards the cathode.

If the view suggested above is accepted, and we assume that copper ions are adsorbed by the particles of the organic colloid, forming complex colloid particles, we may suppose that the complex particles move towards the cathode by a process of cataphoresis and press themselves upon the electrode surface. Here the copper ions gain electrons, and unite to form particles of metallic copper dispersed in a layer of the sticky organic colloid. Afterwards by a secondary process, the metallic copper particles segregate together, and alternate layers of copper and gelatine are formed. There appears to be considerable evidence that the deposit is in a plastic state at the moment of formation, since if the bath is stirred during the process, the surface of the deposit is found to be covered with curious striations caused by the movement of the liquid over the freshly deposited material.[1]

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[1] N. Isgarischew, *Koll. Chem. Beiheft*, **14** (1921), 25.

[2] See, for instance, J. Loeb, *Trans. Faraday Soc.* **16** (1921), Appendix, p. 156.

[3] By C. Grube and V. Reuss, *Zeitsch. Elektrochem.* **27** (1921), 48.

Whatever view is taken, the co-deposition of the colloid substances with the metal—although making the structure finer, smoother and less porous—will inevitably have some effect upon the mechanical character; this effect is usually unfavourable and, if too much colloid is present, the metal is distinctly brittle. Thus whilst small amounts of gelatine added to copper sulphate produce a good shining deposit, larger amounts cause the product to be darker, and render it so brittle that it may peel off from the cathode on drying. Similar effects are noticed in the case of other metals. Not all colloids, however, are equally detrimental, and for any given metal it is usually possible to find a colloid which improves the compactness of the deposit without seriously affecting the mechanical properties. The effect of a colloid addition also depends largely on the quantity added.

In no case is the effect of colloid "addition agents" so welcome as in the deposition of lead.[2] Few metals show a more marked tendency towards dendritic growth; possibly owing to the slow diffusion of the heavy ions, deposition always occurs much more readily at the tips of the growing crystals than at other places: indeed, the lead produced upon a cathode from any ordinary bath is scarcely worthy to be called a deposit at all, being nothing but a hopelessly porous, incoherent mass of dendritic crystals. The "lead tree" obtained when a piece of zinc is suspended in lead acetate solution gives a fair idea of the kind of "coating" one sometimes obtains in lead-deposition.

The difficulties of lead-deposition are rather increased by the fact that the sulphate and chloride—the salts generally employed in the deposition of ordinary metals—are practically insoluble. It is customary to use the silicifluoride or the perchlorate of lead for the deposition of that metal. The addition of gelatine or glue to the silicifluoride bath containing excess of silicifluoric acid, or of peptone to the perchlorate bath, gives a remarkable improvement to the deposit, compact, fine-grained lead being obtained.

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[1] G. Grube and V. Reuss, *Zeitsch. Elektrochem.* **27** (1921), 45. Compare E. Müller and P. Bahntje, *Zeitsch. Elektrochem.* **12** (1906), 317.

[2] H. Freundlich and J. Fischer, *Zeitsch. Elektrochem.* **18** (1912), 885.

Other Addition Agents. The addition of carbon disulphide to the silver-plating bath may here be mentioned; the presence of a small quantity of this substance in the solution in the final stages of plating causes the plating to be remarkably bright. The action is probably similar to that of the colloids; the "bright silver" produced is said to contain sulphur.

The presence of aluminium sulphate in a solution of zinc sulphate causes an improvement in the character of the metallic zinc deposited. Possibly colloidal aluminium hydroxide—produced by the hydrolysis of the aluminium salt—is the cause of this improvement.[1]

There are numerous cases where special addition agents produce a beneficial effect on the deposition of some particular metal; often the reason is uncertain. Iron, for instance, is stated to be deposited in a specially coherent form from a cresol-sulphonate bath.[2] The addition of nitric acid to the copper sulphate bath used in the deposition of copper undoubtedly brightens up the coating produced, although probably the current efficiency drops. The function of nitric acid is said to be that of an oxidizing depolarizer which prevents the evolution of hydrogen in bubbles.[3] It may be mentioned here that, for the deposition of easily oxidized metals, like zinc, the presence of nitric acid—or even of a nitrate—is fatal.

Deposition of Alloys.[4] Of considerable interest is the question of the simultaneous deposition of two metals on the cathode to form an alloy. An instructive example is afforded by the problem of the electrolytic deposition of brass. If a solution containing both zinc sulphate and copper sulphate is electrolysed, only the copper is deposited at the cathode. This is not extraordinary if the interval between the normal electrode potentials is considered :—

$$\mathrm{Cu} \mid \mathrm{CuSO_4} \ +0{\cdot}329 \text{ volts}$$

and

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \ -0{\cdot}770 \text{ volts.}$$

It is true that, when current is passing, the potential of the electrode $\mathrm{Cu} \mid \mathrm{CuSO_4}$ is depressed slightly, but it is hopeless to expect that—whilst any appreciable amount of copper sulphate remains in the solution—the potential will become sufficiently negative for the deposition of zinc.

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[1] See W. D. Bancroft, *Trans. Amer. Electrochem. Soc.* **21** (1915), 233.

[2] S. O. Cowper-Coles, *English Patent*, 10,367, May 3, 1907.

[3] According to A. Classen, "Quantitative Analysis by Electrolysis"; translation by W. T. Hall (Chapman and Hall), p. 100.

[4] See also W. H. Creutzfeldt, *Zeitsch. Anorg. Chem.* **121** (1921), 25.

If, however, we take a bath containing the complex cyanides of the two metals and compare the potentials

$$\mathrm{Cu}\left|\begin{array}{l}\mathrm{CuCN}\ (\tfrac{1}{10}\ \text{gram-equiv. per litre})\\ \mathrm{KCN}\ (1\ \text{gram equiv. per litre})\end{array}\right. = -1{\cdot}169\ \text{volts.}$$

and

$$\mathrm{Zn}\left|\begin{array}{l}\mathrm{Zn(CN)_2}(\tfrac{1}{10}\ \text{gram-equiv. per litre})\\ \mathrm{KCN}\ (1\ \text{gram-equiv. per litre})\end{array}\right. = -1{\cdot}231\ \text{volts}$$

we see that the potentials of the two metals are close together. By electrolysing a cyanide bath containing both metals, therefore, it is possible to effect simultaneous deposition, and a layer of yellow brass is obtained on the cathode.[1]

Similarly, by the electrolysis of an alkaline cyanide bath containing copper and tin, deposits of bronze can be obtained; instead of a cyanide bath, a solution containing complex tartrates may be used.[2]

Not infrequently, the potential required for the deposition of an alloy is less negative than that needed for the deposition of the more reactive constituent. Metallic sodium, for instance, cannot be deposited at any potential obtainable in aqueous solution, but a sodium amalgam is not difficult to produce when a mercury cathode is employed in the electrolysis of a sodium salt solution. This apparent discrepancy—which has already been referred to—is easy to explain. There is a great evolution of heat-energy when metallic sodium is added to mercury, and it is not surprising, therefore, that the energy required for the production of sodium amalgam should be less than that needed for the production of sodium itself.

Similarly, metallic magnesium cannot be prepared from aqueous solutions, but iron-magnesium alloys have been obtained by the electrolysis of a solution containing magnesium chloride and iron sulphate. These alloys, although invariably contaminated with oxide, seem to contain solid solutions of iron and magnesium; they are often pyrophoric.[3]

The proportions in which the two metals are deposited are sometimes rather surprising. A bath containing zinc and nickel sulphates in nearly equal proportions gives an alloy containing far more zinc than nickel[4]; in view of the relative positions of the two metals in the Potential Series, one would have expected that the deposition of nickel would proceed more readily than that of zinc.

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[1] F. Spitzer, *Zeitsch. Elektrochem.* **11** (1905), 345; S. Field, *Trans. Faraday Soc.* **5** (1909), 172; A. L. Ferguson and E. G. Sturdevant, *Trans. Amer. Electrochem. Soc.* **38** (1920), 167.

[2] R. Kremann, C. T. Suchy, J. Lorber and R. Maas, *Monatsh.* **35** (1914), 219.

[3] R. Kremann and J. Lorber, *Monatsh.* **35** (1914), 603.

[4] E. P. Schoch and A. Hirsch, *J. Amer. Chem. Soc.* **29** (1907), 314. See also G. Grube, *Trans. Faraday Soc.* **9** (1914), 216.

Application of Electro-deposition to Analysis. The deposition of metal upon a weighed cathode often constitutes an elegant method for the analytical estimation of a metal. At the present time, the method is applied most often to the analysis of copper ores, but it forms a very convenient analytical process for other metals also.

In a simple form of electro-analytical apparatus, the cathode consists of a weighed cylinder of platinum gauze, the anode being a spiral of stout platinum wire suspended within the cylinder (Fig. 85). The liquid from which the metal is to be precipitated is contained in a beaker just large enough to contain the cathode; the two electrodes are joined through a variable resistance and an ammeter to a pair of accumulators; a voltmeter can be joined in parallel with the electrolytic cell, to show the total E.M.F. applied to the latter.

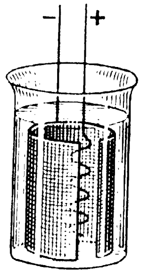

FIG. 85.—Simple Electro-Analytical Apparatus.

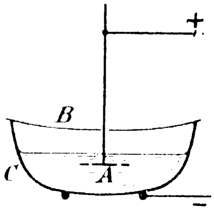

FIG. 86.—Classen's Apparatus.

In another form of apparatus (Fig. 86), a weighed platinum dish, C, having an interior surface which has been roughened by means of a sand-blast, constitutes the cathode; the liquid containing the metal to be estimated is placed in the dish; the anode A consists of a flat perforated disc of platinum furnished with a vertical stem clamped so that the disc itself is just below the surface of the liquid. The dish is covered with a watch-glass B, pierced in the centre to admit the stem of the anode. This is known as Classen's apparatus.

In the simplest forms of electro-analytical apparatus there is no stirring at all except that provided by the oxygen evolved at the anode; the deposition is therefore rather slow, occupying several hours, and the deposit is not so compact as might be desired. If, however, the correct current density and bath-composition is employed, a sufficiently good deposit of any of the ordinary metals can be obtained; when the deposition is complete (which may be ascertained by testing a drop of the liquid for the metal in question) the cathode may be washed, first with water and then with alcohol, dried in a water-oven and re-weighed. The increase of weight naturally represents the metal deposited.

In order to hasten the process, various devices have been introduced for stirring the solution. If the electrodes consist of two concentric gauze cathodes, one inside the other, it is possible to arrange for the anode to rotate with considerable velocity by means of a small motor; an apparatus on this principle has been designed by Sand.[1] An alternative arrangement—which is due to Fischer[2]—involves the use of two stationary cylindrical gauze electrodes, one inside the other, and an independent glass stirrer, which rotates rapidly within the inner electrode. In one form of the Classen apparatus it is possible to cause the disc anode to revolve during the deposition.

Either of these forms of apparatus allow the complete deposition of the metal in 10–30 minutes, and naturally yield a far more coherent deposit than is obtained without mechanical stirring. Copper—for instance—comes down from a sulphate solution containing nitric acid as a compact and glittering coat instead of a dull reddish porous deposit. Bismuth, a metal which can scarcely be estimated at all with an unstirred solution, on account of the non-coherent character of the deposit produced, can be made to give a quite satisfactory weighable deposit when the liquid is kept in motion.

Whether the deposition is conducted from a stirred or unstirred bath, care must be taken to secure conditions of working which ensure complete deposition of pure metal, in an adherent form which can be readily washed, dried and weighed. The exact instructions laid down in the practical handbooks should be rigidly followed.[3] In many cases, it is advisable to work from a bath containing the metal as a complex salt. The following table shows the chemical nature of the solutions from which the complete electro-deposition of different metals can be conveniently conducted:—

Silver	Sulphate solution containing free nitric acid.
Mercury	
Copper	
Bismuth	Complex tartrate solution.

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[1] H. J. S. Sand, *Trans. Chem. Soc.* **91** (1907), 373; **93** (1908), 1572.

[2] A. Fischer, *Zeitsch. Elektrochem.* **13** (1907), 469.

[3] For the processes using unstirred liquid, see A. Classen, "Quantitative Analysis by Electrolysis"; translation by W. T. Hall (Chapman and Hall). For the rapid processes see A. Fischer, "Electroanalytische Schnellmethoden" (Enke).

Antimony Tin	Solution containing sulphides and cyanides.
Nickel Iron Zinc	Complex oxalate solution.

But, in every case, there are several alternative methods ; zinc, for instance, has been successfully determined from a solution of a zincate containing free sodium hydroxide.

When only one metal is present in the solution, electro-analysis presents little difficulty. If two or more metals are present in the solution, it is necessary to ensure that only one is deposited at a time. If the metals are widely separated in the Potential Series, this can usually be done without special apparatus. For instance, if the solution contains copper and zinc as sulphates, it is possible to deposit copper free from zinc, as we have seen ; to make the separation complete it is best to add a little nitric acid to the solution—the presence of which will prevent entirely the deposition of zinc. After the coppered cathode has been weighed, it is possible to drive off the nitric acid from the solution by evaporation with sulphuric acid on the water-bath, and to deposit the zinc remaining from a complex oxalate solution upon the coppered cathode ; it is destructive to the platinum of the electrode to deposit zinc directly upon that metal.

In general, however, where two metals are present in the solution, it is necessary to control the potential at the cathode by means of an auxiliary electrode and a potentiometer. A "normal calomel" electrode is useful in some cases as the "auxiliary electrode," but, since the solution employed is usually acid, a mercurous sulphate electrode—contained in the same sort of vessel as is used for the "calomel electrode"—is preferable. Whichever is employed the end of the tube of the auxiliary electrode is introduced into the beaker, close up against the cathode ; the auxiliary electrode and the cathode are then joined to a potentiometer, by means of which the single potential at the cathode surface can be determined from time to time during the electrolysis. The variable resistance on the main circuit is adjusted so that the cathodic P.D. is always sufficiently depressed to cause the deposition of one metal, but not sufficiently depressed to involve the precipitation of the other. For instance, if the solution in the beaker contains salts of copper and mercury acidified with nitric acid, and the auxiliary electrode consists of

$$\mathrm{Hg}\left|\begin{array}{l}\mathrm{Hg_2SO_4}\text{ in}\\ \mathrm{2N\ H_2SO_4}\end{array}\right.$$

the resistance of the main circuit should be adjusted during electrolysis so that the potentiometer indicates 0·0 to 0·15 volt, the temperature of the solution being 100° C. Under these circumstances only mercury can be deposited; no copper could come down unless the P.D. were to reach 0·3 volt. After the whole of the mercury has come down, and the cathode has been weighed, the solution containing copper is electrolysed separately, the cathodic potential being depressed sufficiently to allow the deposition of that metal.[1]

Some metals, like manganese and lead, produce an insoluble dioxide (MnO_2 and PbO_2) in a hydrated form on the anode when a solution of a salt is electrolysed under certain conditions. This fact has been utilized for the estimation of these metals.

The extensive use of the electro-analytical methods is somewhat limited by the price of platinum. By designing the apparatus in an appropriate manner, the amount of platinum needed can be considerably reduced,[2] but the cost still remains considerable. Much work has been devoted to the problem of finding a cheaper electrode-material. As regards the construction of the cathode, many cheaper materials, such as silver,[3] tantalum,[4] or even graphite,[5] are suitable for use under specified conditions. There seems to be no cheap material which will form a really satisfactory substitute for use as an anode, but it is stated that an alloy of gold, silver and copper, plated with platinum, can be used in the place of solid platinum.[6]

Summary. The deposition of fairly noble metals like copper and silver will proceed at high current efficiency; but, in the case of more reactive metals like iron and zinc, current is likely to be wasted in the production of hydrogen, especially if the solution is unduly acid. However, the evolution of hydrogen is opposed by overpotential, and zinc—which has a high overpotential value at low temperatures—may be deposited at high current efficiency so long as the solution is kept cool.

Evolution of hydrogen from a bath originally neutral tends to render it alkaline, and may give rise to the co-precipitation of hydroxides at the cathode, causing the deposit of metal to be spongy. It is usually advisable to keep the bath acidified with some weak acid, unless a cyanide, tartrate, or other reagent which would act as a solvent for hydroxides is present.

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[1] For further details see H. J. S. Sand, *Trans. Chem. Soc.* **91** (1907), 393.

[2] F. A. Gooch and W. L. Burdick, *Amer. J. Sci.* **34** (1912), 107.

[3] H. E. Medway, *Amer. J. Sci.* **18** (1904), 180.

[4] O. Brunk, *Chem. Zeit.* **36** (1912), 1233.

[5] J. W. Turrentine, 7th *Int. Cong. App. Chem.* (1909) Section 1, p. 177.

[6] K. Arndt, *Elektrotech. Zeitsch.* **42** (1921), 345.

Slow deposition of metal at low current density means only a small departure from the equilibrium value of the potential, and hence the formation of few nuclei on the cathode, the deposit produced being therefore coarsely crystalline, loose and rough. A higher rate of deposition involves greater polarization, and produces a finer, smoother and more coherent form of metal. If, however, the rate of deposition becomes so great that exhaustion of metallic ions occurs, the effect is unfavourable. This can be avoided by employing a concentrated solution and by violently agitating the bath.

If, as in plating, violent stirring is not practicable, high polarization (and hence fine deposits) can be produced by working from a complex salt solution (e.g. a cyanide solution), in which the concentration of simple cations is low. The presence of certain colloids likewise improves and brightens the deposit, probably owing to the formation of complexes. In the presence of colloids, the structure becomes laminated or scaly (the scales being parallel to the cathode surface) instead of consisting of finger-like crystallites (perpendicular to the cathode surface); apparently the colloid is co-deposited with the metal, by the cataphoresis of complex colloid particles, forming a deposit which is quite plastic at the moment of formation. Many colloids have a bad effect upon the mechanical qualities of the metal deposited.

The adhesion of the deposit to the cathode is better if the cathode is roughened and if it consists of a soft metal, or one which will alloy with the metal being deposited. Metals like iron and nickel, which absorb hydrogen, are deposited in a brittle condition, and tend to crack and to peel off in a tight roll, an occurrence which shows that the deposit is in a state of tension.

Electro-deposition is used in the analytical estimation of metals. The deposition is quicker, and the deposit is brighter and more compact, if the solution is vigorously stirred. Through the control of the cathodic potential, by means of an auxiliary electrode and a potentiometer, the separate deposition of two or more metals from a mixture is possible.

CHAPTER XII

THE DISSOLUTION OF A METALLIC ANODE

The two possible views held regarding the character of the reaction at the anode were briefly referred to in Chapter V; it is necessary, at the present stage, to consider the matter in further detail.

When a zinc plate is made the anode in an electrolytic cell containing a solution of zinc chloride, or any other soluble chloride, various changes may occur. The simplest reaction is the passage of the metallic atoms into the ionic condition, thus

$$(1)\ \mathrm{Zn} = \mathrm{Zn}^{\cdot\cdot} + 2e.$$

An alternative reaction is the discharge of chlorine ions on the zinc surface

$$(2a)\ 2\mathrm{Cl}' = 2\mathrm{Cl} + 2e.$$

But since zinc is a reactive metal it will at once combine with the chlorine producing zinc chloride

$$(2b)\ \mathrm{Zn} + 2\mathrm{Cl} = \mathrm{ZnCl}_2,$$

and the zinc chloride will dissolve in the liquid, and dissociate into ions, thus

$$(2c)\ \mathrm{ZnCl}_2 = \mathrm{Zn}^{\cdot\cdot} + 2\mathrm{Cl}'.$$

If we add up the three reactions (2*a*), (2*b*) and (2*c*) we get

$$\mathrm{Zn} = \mathrm{Zn}^{\cdot\cdot} + 2e$$

identical with reaction (1). Thus, as far as can be seen at present, both changes lead to the same final result, the passage of the zinc into the dissolved state, and no conclusion can be drawn from experimental investigation as to whether it occurs directly or in three stages.[1]

If, however, the anode consists not of zinc, but of silver, little or no silver passes into solution, but the surface of the anode becomes covered with a layer of insoluble silver chloride. This result is most simply explained on the assumption that chlorine ions are discharged, and that the chlorine then combines with the silver, the charges being analogous to reactions 2a and 2b.

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[1] Reasons for thinking that the discharge of the anion is, in most cases, the primary anodic reaction are given by O. Sackur, *Zeitsch. Elektrochem.* **14** (1908), 612.

Finally if the anode consists of a "noble" metal, such as platinum, which does not combine with chlorine at any very appreciable velocity, chlorine gas is evolved; here there seems to be no alternative but to adopt the idea of the discharge of the anion, according to equation 2a.

Similar results are obtained when a solution of a sulphate is electrolysed. If the anode consists of a reactive metal like zinc, the sulphate of which is soluble, the zinc passes into solution. If the anode metal has an insoluble sulphate, as in the case of lead, it becomes covered with a solid crust of sulphate, which, as it becomes thicker, may actually shield the metal below it from further attack, although as we shall see it does not usually prevent other reactions from occurring at the electrode. Finally, if the anode consists of a noble metal, like platinum, the anions $(SO_4)''$ are discharged, according to the equation

$$(3a)\ SO_4'' = SO_4 + 2e$$

and we usually obtain oxygen by the secondary reaction

$$(3b)\ SO_4 + H_2O = H_2SO_4 + O.$$

The evolution of oxygen at an anode always tends to leave the solution around the electrode acid, just as the evolution of hydrogen at a cathode renders the solution alkaline. The production of oxygen may also occur in another way, namely by the direct discharge of hydroxyl ions,

$$(4a)\ 2OH' = 2OH + 2e$$
$$(4b)\ 2OH = H_2O + O.$$

This reaction is, of course, more likely to occur in alkaline solutions, in which the concentration of hydroxyl is considerable; but hydroxyl also occurs to a small extent in neutral, or even in acid, solutions, owing to the ionization of water. If the solution is neutral when electrolysis commences, the discharge of hydroxyl ions will leave hydrogen ions in excess and here again the solution will be rendered acid.

The production of oxygen at an anode may have important results even where it is not evolved in gaseous form. Take, for instance, the case of a lead anode immersed in sulphuric acid solution. At first the effect of electrolysis is to cover the lead with a coat of white insoluble lead sulphate. After a time the coating is thick enough practically to shield the lead below from further attack. Since the formation of sulphate is prevented, the anodic potential will—if the applied E.M.F. is sufficient—rise until it is high enough for the production of oxygen. Owing to "over-potential," the oxygen will not at first appear as gas, but will act upon the lead sulphate converting it to the "puce-coloured" peroxide, according to some such reaction as,

$$PbSO_4 + H_2O + O = PbO_2 + H_2SO_4.$$

Only when practically all the sulphate has been converted to peroxide will the anode become so supersaturated with oxygen that the evolution of the gas in bubbles will occur.

Here the product of oxidation, lead peroxide, is a well-known substance which can be prepared in other ways and which has an oxygen-content closely approximating to the simple formula PbO_2; the peroxide film has a measurable thickness, and the marked colour-change which accompanies its production leaves little doubt as to the character of the product of anodic polarization. But in other cases, anodic polarization—although producing a very marked change in the electrochemical properties of a metal—leads to very little change in the appearance.

Consider, for example, the polarization of a platinum anode. When the anodic potential is raised as high as 1·23 volts, the surface is saturated with oxygen. But—owing to "overpotential"—no evolution in bubbles occurs until the potential is raised to about 1·5 or 1·7 volts; the exact point depends on the surface condition of the electrode, a higher potential being needed for bright platinum than for blackened platinum. Evidently, between 1·23 volts and 1·50 volts, the platinum is supersaturated with oxygen. The oxygen is apparently firmly fixed in the metal, because, if the current is turned off, the electrode maintains its elevated potential for some considerable time. Many chemists regard the permanent character of this polarization as an indication that an oxide has been produced in—or upon the surface of—the electrode, but it is unlikely that there is any well-defined oxide of constant composition present. The oxygen content of the electrode seems to vary gradually with the anodic potential maintained during the polarization process, and also with the time during which the polarizing current has been allowed to flow; it has been suggested that a solid solution of an oxide (possibly PtO_3) in the platinum is formed at the polarized electrode and that the proportion of the oxide present in the solid solution determines the potential of the electrode.[1] When the polarizing current is turned off, and the electrode is allowed to rest, it gradually loses oxygen, the potential at the same time gradually dropping; if immersed in a solution through which oxygen is bubbled, the electrode retains its high potential wonderfully well; it may take as long as ninety days to drop to 1·1 volts. Such a continuous drop is quite consistent with the theory that an oxide is present dissolved in solid solution in the metal; but it is, perhaps, rather more simple to imagine that an adsorbed layer of oxygen atoms is present on the platinum surface, the surface-concentration of the atoms being the determining factor of the potential. Such a layer can rightly be regarded as an oxide-film, since the forces binding the oxygen atoms to the metal are of the same character as chemical forces; but the film will not correspond to any oxide which we know in the massive form, but must be regarded, essentially, as an oxide film of variable composition.

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[1] F. Foerster, *Zeitsch. Phys. Chem.* **69** (1909), 236; G. Grube, *Zeitsch. Elektrochem.* **15** (1909), 769; **16** (1910), 621; G. Grube and B. Bulk, *Zeitsch. Elektrochem.* **24** (1918), 237. Most of these researches, it should be noticed, refer to "black" (platinized) platinum electrodes.

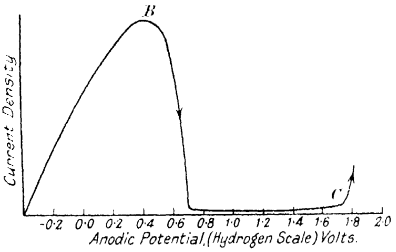

FIG. 87.—The Anodic Behaviour of Iron in $\frac{N}{10}$ Sulphuric Acid.

Passivity. Of especial interest is the behaviour of an anode consisting of iron, cobalt or nickel. Here, when the current density is low—and consequently when the anodic potential differs but little from the equilibrium value—the metal behaves in much the same way as zinc, and the electrode can be regarded as an ordinary "soluble anode." But, if the potential is raised so that the production of oxygen in the anode becomes appreciable, the whole nature of the electrode changes, and it shows a behaviour similar to that of platinum; the metal acquires a "noble" character, and this noble character survives for an appreciable time even after the current has been turned off.

The behaviour, under increasing polarization, of an iron anode surrounded by $\frac{N}{10}$ sulphuric acid is shown in Fig. 87.[1] At low current densities, the potential at the dissolving anode is only a little above the equilibrium value. Under such circumstances, the current density being small, the rate of dissolution is correspondingly low; but nevertheless practically all the current which does pass is devoted to the dissolution of the anode. If, however, by increasing the E.M.F. applied to the electrolytic cell and so increasing the current density, we attempt to hasten the dissolution still further, an entirely contrary result takes place. At a certain limiting current density (point B), the anode potential reaches a value at which the accumulation of oxygen upon the electrode becomes important; at that point the change produced on the surface of the electrode begins to interfere with the anodic dissolution of the metal; the current begins to diminish and if time is allowed drops practically to nothing. Nor does the current begin to pass again until the anodic potential is made high enough to allow the evolution of oxygen in gaseous form (point C), and beyond that point practically all the current that passes is devoted to the evolution of oxygen, the anodic dissolution of the metal being almost negligible. The electrode thus functions as an "unattackable electrode," like a platinum electrode, and the metal is said to be "**passive.**"

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[1] Founded on results given by C. Fredenhagen, *Zeitsch. Phys. Chem.* **43** (1903), 1. The curves given by E. P. Schoch and C. P. Bandolph, *J. Phys. Chem.* **14** (1910), 719, are somewhat different, the experimental method employed being somewhat different, but the same general conclusions can be drawn from both sets of curves.

If the current be shut off, the iron quickly returns to its original "active" state, the potential dropping to a negative value similar to that which was shown before the metal became passive; but this return to the active state takes an appreciable time. If nitric acid, in the place of sulphuric acid, is employed, the potential remains elevated, and the metal retains its acquired "noble" properties for a period varying between one and twenty minutes. Then suddenly the potential "tumbles" to a negative value, and the metal becomes active. If the E.M.F. is applied again before the "tumble" has occurred, the iron will function as an "insoluble anode"; if it be applied after the "tumble" has taken place, the iron will be found to have regained its original power to dissolve quantitatively at low current densities.

Evidently, therefore, the change in the nature of the electrode is of a character which survives after the polarization agency is removed. If the change consists in the formation of an oxide film, the time which elapses before the electrode becomes active must be regarded as the time taken by the acid to dissolve the oxide film. It is noteworthy that in neutral or alkaline liquids, in which the oxide would be almost insoluble, the iron remains passive for a much longer period after the polarizing E.M.F. is shut off. In order to restore the passive metal quickly to the original "active" state, it is always possible to pass current in the contrary direction, that is to polarize the metal cathodically. The hydrogen liberated during cathodic polarization effectually removes the oxygen from the surface, and, when the reverse current is shut off, the potential is as low as that of the metal at the beginning of the operation, or possibly lower. The metal is now once more active, and is capable of efficient dissolution when it is once more made the anode at a low current density. Thus, whilst anodic treatment may cause the production of the passive state, cathodic treatment is favourable to the restoration of activity.

Since the passivity of the polarized electrode is believed to be due to the presence of oxygen on the surface, it is not surprising to find that the "limiting current density" beyond which one cannot pass without causing passivity, is much lower in alkaline solutions where the hydroxyl concentration is high, than in the presence of acids. Thus alkalis are favourable to the passive state, acids to the active state. Likewise the presence of oxidizing agents—especially nitrates or chromates—favours passivity, and the presence of reducing agents favours the restoration of the active condition; this is also readily understood. The approximate values of the limiting current density above which passivity sets in—if sufficient time is allowed—is shown by the following table [1]:—

Electrolyte.	**Approximate Limiting Current Density.** Milliamps per sq. cm.
N Potassium sulphate, N/100 sulphuric acid	350
N Potassium sulphate .	300
N Potassium sulphate, $\frac{N}{100}$ potassium hydroxide	250
N Potassium sulphate, $\frac{N}{10}$ potassium hydroxide	10
$\frac{N}{10}$ Potassium hydroxide .	Very low
$\frac{N}{10}$ Potassium nitrate	50 (vague)
$\frac{N}{30}$ Potassium dichromate .	Very low

It should be noted that the appearance of passivity is much less likely with a warm solution than with a cold one. This is readily understood, since the normal reaction

$$Fe \longrightarrow Fe^{\cdot\cdot} + 2e$$

will proceed much more readily at high temperatures than at low ones, and hence the accumulation of oxygen will not occur.

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[1] Based on the data given by E. P. Schoch and C. P. Bandolph, *J. Phys. Chem.* **14** (1910), 719.

Very important is the action of chlorides, bromides and iodides in keeping a metal "active"; it is very difficult to render a metal passive by anodic polarization in the presence of chlorides. The discharge of Cl′ ions, unlike the discharge of $(SO_4)''$, $(NO_3)'$ or $(OH)'$ ions, does not lead to the accumulation of oxygen on the surface of the iron. An iron electrode which has been rendered passive by polarization in a sulphate solution commences to dissolve again if a small quantity of chloride is added to the solution. The actions of chlorides in restoring activity to a "passive" metal is a very general one, and is not confined to the case of iron. The chlorides do not appear to dissolve the protective film, but they do appear to loosen it, preventing it from clinging to the electrode and thus rendering it non-compact and non-protective. The action may perhaps be connected with the known "peptizing" effect of metallic chlorides upon hydroxides; the present writer has put forward an explanation based on considerations of surface energy.[1]

It is noteworthy that the process of passivity requires a certain time. If an E.M.F. sufficient to cause a current density exceeding the limiting value is applied to an electrolytic cell furnished with an iron anode, the iron goes into solution at first, but, gradually—as oxygen commences to accumulate upon the anode—it begins to dissolve less readily, and finally becomes completely passive. If the E.M.F. is not sufficient to cause evolution of oxygen in gaseous form, the current sinks to zero: if, on the other hand, the E.M.F. is sufficient to cause evolution of oxygen in bubbles, a current continues to pass, but is concerned almost wholly with the production of the gas.

The time needed to cause passivity is greatly reduced if dissolved oxygen is already present in or around the anode.[2] This is, perhaps, the cause of an interesting fact noted by Heathcote,[3] who rendered an iron electrode passive by anodic treatment in sulphuric acid, and then allowed it to regain activity by shutting off the current; when it was active, he turned on the current, and made it passive again, repeating the operation several times. He found that on each successive occasion, a shorter time was needed to make the iron passive; it was possible, as he expressed it, "to teach the iron to become passive." Presumably a certain amount of dissolved oxygen remained in the solution (and possibly in the electrode) even after the electrode had become active, and this oxygen helped in making the iron passive when the current was again turned on.

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[1] U. R. Evans, *Trans. Faraday Soc.* **18** (1922), 1.

[2] H. G. Byers and S. C. Langdon, *J. Amer. Chem. Soc.* **36** (1914), 2004.

[3] H. L. Heathcote, *J. Soc. Chem. Ind.* **26** (1907), 902.

Very striking is the phenomenon of "**periodicity,**" so often noticed in experiments on passivity. It only occurs when the hydrion concentration and the E.M.F. applied to the cell fall within certain limits. Supposing the iron anode is first of all active; a considerable current passes at first, but this renders the iron passive and the current falls off. The evolution of oxygen then commences and causes a highly acid layer in the solution close to the anode. After some minutes the acid causes the electrode to become active again; the iron then commences once more to dissolve, the current rises, and the evolution of oxygen ceases. Soon, however, passivity sets in a second time, and the alternations between activity and passivity continue indefinitely. The periodicity may be recognized either by the alternate rise or fall of the reading of an ammeter in series with the cell, or by the periodical evolution of oxygen gas, which occurs only when the iron is in the passive state.

It is evident that—in general—the equilibrium potential of an iron electrode depends, not merely on the concentration of iron ions in the solution in which it is immersed, but to an even greater extent on the "**previous history**" of the electrode. If the electrode has lately been subjected to cathodic polarization, the potential will be low—probably between $-0{\cdot}4$ and $-0{\cdot}7$ volts—and the metal will be active. If it has been subjected to anodic polarization, the potential will be high (positive) and the metal will be passive. The actual value of the potential of passive iron depends on the nature of the anodic treatment, and will—like the potential of platinum—be made higher by the presence of strong oxidizing agents in the liquid in which the iron is immersed. In fact, a passive electrode should not be regarded as an iron electrode at all, but rather as an oxygen electrode.

It is evident that cathodically polarized iron contains hydrogen, and it can be stated definitely that iron containing hydrogen is active. Likewise anodically polarized iron contains oxygen; iron containing oxygen is therefore passive. The question naturally arises: Is iron containing neither hydrogen nor oxygen active or passive? It would seem rational to expect it to be active, but the theory has been advanced by certain German chemists that pure iron is—in itself—passive, and only becomes active in the presence of hydrogen; this is called the "**hydrogen theory**" of passivity,[1] whilst the alternative view—that pure iron is active, and only becomes passive under the influence of oxygen—may be called the "**oxygen theory.**"[2]

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[1] G. C. Schmidt, *Trans. Faraday Soc.* **9** (1914), 257; W. Rathert, *Zeitsch. Phys. Chem.* **86** (1914), 569.

[2] E. P. Schoch, *Trans. Faraday Soc.* **9** (1914), 274; F. Flade, *Zeitsch. Phys. Chem.* **76** (1911), 513.

It is not so easy to decide between these two theories by direct experiment as one might expect. Iron does not give up its occluded gases at all readily, and, although by heating in an inert gas or *in vacuo*, a large proportion is evolved, it is difficult to ensure that the last traces have been eliminated. Most of the evidence adduced on either side is open to criticism by the supporters of the rival theory. Active iron, after heating *in vacuo*, is found, still to be active, a fact which appears to support the "oxygen theory," on the assumption that the whole of the gases are expelled by the treatment.[1] Likewise, after a clean surface of iron has been obtained by grinding, the iron—whether passive or active before the process—is always found to be active.[2] It must be admitted that these arguments are not conclusive, but they certainly seem to favour the "oxygen theory." More convincing—in the opinion of the present writer—is the argument founded on the comparative behaviour of different metals. Metals like iron and nickel having oxides soluble in acid but not in alkali tend to become active in acid solution and passive in alkalis. Metals like molybdenum and tungsten, the principal oxides of which are soluble in alkalis, tend to become passive in acids but active in alkalis. This would certainly seem to support the view that passivity is due to something in the nature of an oxide film. The oxygen theory will therefore be adhered to throughout this book.[3]

If it is agreed that the more or less lasting change brought about in iron by anodic polarization is due to oxygen, it is necessary to inquire further into the nature of the protective film which retards or prevents the dissolution of the metal itself, whilst allowing of the discharge of anions and the production of oxygen on the surface. The early view that a film of some known oxide, such as the magnetic oxide (Fe_3O_4), exists upon the surface was extremely natural. It has, however, been demonstrated that the optical properties of the iron surface generally undergo no change when the iron becomes passive—although the presence of an oxide-film of any appreciable thickness would certainly cause such a change.[4] There does not appear, however, to be any valid objection to imagining that the protective film consists of a layer of adsorbed oxygen atoms, or possibly molecules, firmly attached to the surface. As in the case of platinum, the surface can then be regarded as coated with an oxide-film of variable composition, but not a film of any oxide known in the massive condition. The firmly attached oxygen atoms would not prevent the discharge of $(SO_4)''$ or $(OH)'$ ions on the outside of the layer, the liberated electrons passing through the oxygen layer into the metal below; thus the layer would allow those electrodic reactions to take place which give rise to the evolution of oxygen. On the other hand, the passage of iron ions in the opposite direction would probably be hindered, for the size of an iron ion is very much larger than that of an electron. Thus at a passive electrode, the change

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[1] F. Flade and H. Koch, *Zeitsch. Elektrochem.* 18 (1912), 335.

[2] W. Muthmann and F. Fraunberger, *Sitzungsber. Bayer. Akad.* 34 (1904), 201.

[3] Some of the arguments advanced for the different theories of passivity are summarized by G. Senter, *Trans. Faraday Soc.* 9 (1914), 203, who is inclined to prefer the "Hydrogen Theory." See also J. Stapenhorst, *Zeitsch. Phys. Chem.* 92 (1917), 238.

[4] W. J. Müller and J. Königsberger, *Zeitsch. Elektrochem.* 13 (1907), 659 ; 15 (1909), 742. See, however, P. Krassa, *Zeitsch. Elektrochem.* 15 (1909), 490.

$$Fe = Fe^{\cdot\cdot} + 2e$$

would become extremely slow. That the anodic dissolution of a passive anode does not entirely cease, but continues to occur very slowly for an indefinite time, has been demonstrated by more than one observer.[1] It is stated that the current efficiency of dissolution in the passive state is often about 1 per cent., whilst that in the active state is over 99 per cent.[2] Additional evidence that there is something in the nature of an obstructive film upon passive iron is afforded by investigations upon the photo-electric effect. Like all metals, iron gives off electrons when exposed to ultra-violet light, but it has been found that the effect greatly declines when the iron becomes passive.[3]

Whilst many chemists regard the protective influence of the oxygen layer as due to purely mechanical causes, others[4] prefer to look upon the oxygen in the anode as a "negative catalyst," which exerts an unfavourable influence of a chemical character upon the change

$$Fe = Fe^{\cdot\cdot} + 2e.$$

Possibly the film of adsorbed oxygen may act as a "poison" just as a film of adsorbed arsenic or sulphur upon a platinum catalyst acts as a "poison," hindering reactions which would otherwise take place at the platinum surface. The theory is somewhat vague; but it has been pointed out in support of it that, in the electrolysis of potassium iodide between platinum electrodes, the presence of a little oxygen in the anode greatly interferes with the production of iodine.[1]

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[1] See H. L. Heathcote, *J. Soc. Chem. Ind.* **26** (1907), 906.

[2] C. A. Lobry de Bruyn, *Rec. Trav. Chim.* **40** (1921), 30.

[3] H. S. Allen, *Trans. Faraday Soc.* **9** (1914), 247. Compare W. Frese, *Zeitsch. Wiss. Photo.* **21** (1921), 37.

[4] G. Grube, *Trans. Faraday Soc.* **9** (1914), 214. For other examples of apparent negative catalysis at an electrode, see G. Reichinstein, *Trans. Faraday Soc.* **9** (1914), 228.

Chemical Passivation of Iron.[2] Although the passivity of metals is most conveniently studied by observing the sudden rise of potential caused by anodic polarization, yet it is extremely easy to make iron passive by immersing it in an oxidizing agent without the use of the electrical current. When iron is immersed in concentrated nitric acid (specific gravity 1·3 to 1·4) it dissolves at first, but the velocity of attack soon drops, and finally the iron becomes passive. It is noteworthy that only concentrated acid (specific gravity exceeding 1·25) produces this passivity; nitric acid of gravity below 1·25 slowly renders passive iron active. The activation is however usually slow, and Heathcote proposes the immersion of iron in nitric acid of specific gravity 1·2 as a test to decide whether a given piece of iron is active or passive. If active, the iron at once evolves gas when dropped into the acid; if passive, the iron is unaffected by the dilute acid for several hours—after which it becomes active, and commences to dissolve.

Immersion in other oxidizing agents, such as chromic acid or potassium permanganate, often renders iron and other metals passive. Periodicity is observed not infrequently in the "chemical passivation" of metals.

Various experiments are described by Heathcote which seem to prove that the passivation by immersion in a solution of an oxidizing agent may—in many cases—be really electrical in character. Iron immersed in nitric acid of gravity 1·3—that is, just above the limiting concentration—only becomes passive very slowly. But if the iron is touched by a piece of lead or gold—metals which stand above iron in the Potential Series—it becomes passive at once; presumably a short-circuited cell of the type

Iron | Nitric Acid | Lead (or Gold)

is produced, in which the iron functions as anode, and passivation quickly sets in. On the other hand, if the passive iron is afterwards touched with a stick of zinc, the iron becomes active again. For zinc occurs below iron in the Potential Series, and in the cell

Zinc | Nitric Acid | Iron,

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[1] The present writer has suggested that the presence of the oxygen film linking the metal to the solution decreases the surface energy of the interface, Metal | Solution, and thus renders the system more stable; the increased stability is shown by the "ennoblement" or "passivity" of the metal. See U. R. Evans, *Trans. Faraday Soc.* **18** (1922), 1.

[2] H. L. Heathcote, *J. Soc. Chem. Ind.* **26** (1907), 899. A very large number of most interesting experiments are described in this paper.

the iron is cathode, and the cathodic polarization renders it active once more.

Very interesting are the effects of bringing into contact below the surface of a liquid two iron rods, one active and one passive. Evidently, the potentials at the surfaces of the two rods will be different, and the short-circuited cell

Active Iron	Electrolyte	Passive Iron

will produce a current, which will, in general, continue until the oxygen concentration upon the surface of both becomes equal; in other words, until both are active or both passive. As to which of these two events will occur depends on various factors, notably on the composition of the electrolyte; if the liquid is nitric acid, the active rod will usually become passive, whilst, if the electrolyte is sulphuric acid, the passive one will become active.

Passive iron differs considerably in chemical properties from ordinary iron. As stated above, it does not dissolve in nitric acid of specific gravity 1·2; nor does it precipitate metallic silver from silver nitrate solution.

Passivation of Other Metals. Other metals which occur close to iron in the periodic table show a similar tendency to become passive, when anodically polarized above a certain limiting current density, or when immersed in oxidizing agents. Often exposure in the air causes a marked rise in the equilibrium potential, whilst the scraping of the surface causes the potential to assume a more "active" value.[1]

Nickel becomes passive more easily than iron; if the anodic method is employed, passivity sets in at a very much lower current density; moreover, the metal remains passive for a longer time, other things being equal, when the polarizing current is shut off. On the other hand, **cobalt**[2] requires a higher current density than iron before it becomes passive.

The passivity of nickel is of some importance in nickel plating. It is customary in a nickel plating bath to use anodes of nickel, which should dissolve as the current passes and—under conditions of perfect current efficiency—supply exactly as much nickel to the bath as has been lost by the deposition upon the cathode. So long as the anodic current density is very small, the anodes usually dissolve tolerably well; but, if at any moment it becomes excessive, they turn passive, and practically cease to dissolve. Nor does the dissolution recommence when the current density is lowered again to the proper limits. Therefore, when once passivity has set in, the bath becomes impoverished of nickel and some fresh nickel salt must be added; incidentally the evolution of oxygen at the anodes tends to render the bath more acid, and so interferes with the current efficiency of the deposition at the cathode. Chlorides are often added to the plating bath to reduce the danger of passivity.

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[1] W. Muthmann and F. Fraunberger, *Sitzungsber. Bayer. Akad.* **34** (1904), 201.

[2] H. G. Byers and C. W. Thing, *J. Amer. Chem. Soc.* **41** (1919), 1902; H. G. Byers, *J. Amer. Chem. Soc.* **30** (1908), 1718.

The case of **chromium**[1] is a curious one, because here there is a high oxide (CrO_3) which is quite soluble in water. At a temperature of 100°, a chromium anode dissolves quantitatively in potassium chloride solution producing blue $Cr^{\cdot\cdot}$ ions; from the blue solution produced, the salt $CrCl_2$ can be obtained by crystallization. If, however, the same experiment is tried at ordinary temperatures, even a very low current density is sufficient to make the chromium passive, and dissolution does not take place. Evidently the oxygen accumulation on the electrode surface becomes sufficient to interfere with the entry of the metal into the ionic state. If, however, the E.M.F. applied to the cell be made high enough, the chromium starts to dissolve once more, but now as the yellow oxide CrO_3 (or its hydrate, chromic acid, H_2CrO_4); evidently the dissolution will only commence when the anodic potential is so elevated that the oxygen concentration becomes sufficient to produce this high, endothermic oxide. It requires a potential of at least + 1·1 volts to oxidize the chromium to the oxide CrO_3. If there is present in the solution an anion which can be discharged at a lower potential, the accumulation of oxygen in the chromium will never become sufficient for the formation of the soluble oxide CrO_3. Now the iodine ion, I', is discharged at all potentials exceeding about + 0·6 volts, and it is not surprising therefore that when a chromium anode is used in a solution of cold potassium iodide, yellow chromic acid is not formed, and the anode remains unattacked.

For some reason, the failure of chromium to be dissolved anodically in a solution of potassium iodide is looked upon by supporters of the "hydrogen theory" of passivity as a fact that cannot be explained upon the "oxygen theory"; in the opinion of the present writer, the explanation just given[2] is far more satisfactory than any that the supporters of the "hydrogen theory" have to offer.

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[1] W. Hittorf, *Zeitsch. Phys. Chem.* **25** (1898), 729; **30** (1899), 481; **34** (1900), 385.

[2] Practically identical with the view taken by C. W. Bennett and W. S. Burnham, *Trans. Amer. Electrochem. Soc.* **29** (1916), 252.

Chromium in the active state thus dissolves to produce the blue divalent chromous ion (Cr˙˙); chromium in the passive state dissolves to form the yellow chromic acid, or a chromate, in which the metal is hexavalent. In the active condition, dissolution can occur at a negative potential; in the passive condition, dissolution requires a potential made highly positive by means of an externally applied E.M.F. Thus active chromium behaves as a metal similar to zinc or cadmium, between which it falls in the Potential Series, whilst passive chromium behaves as a highly noble metal similar to platinum. The occurrence of the active or passive condition is determined largely by the solution in which it is immersed, oxidizing agents—even dissolved oxygen—being favourable to the passive condition. But temperature is also an important factor, and, as stated above, a chromium anode generally remains active in potassium chloride solution at 100°, but becomes passive in the same solution at ordinary temperatures. Thus the cell

$$\mathrm{Cr} \mid \mathrm{KCl\ solution} \mid \mathrm{NaNO_3} \mid \mathrm{AgNO_3\ solution} \mid \mathrm{Ag}$$

furnishes at 100° a continuous current, with an E.M.F. of about a volt; whilst current is being generated, the chromium goes into solution as the blue chromium ion (Cr˙˙). But, if the same cell be used at ordinary temperatures, the chromium soon becomes passive, and the current practically ceases. If by applying an external electric battery (a couple of ordinary Daniell cells, for instance) we force current through the cell, the chromium will be seen to dissolve as yellow chromic acid, not as a blue chromous salt.

The other metals of Group VIA also display very diverse properties according to whether they are in the active or passive state. The potential of **tungsten**, for instance, may vary from $-0{\cdot}676$ volts, in its most active condition, to $+1{\cdot}013$ volts, in its highly passive condition.[1] Moreover, in the same group, we meet with a curious departure from the general rule that acids favour activity, and alkalis passivity. **Molybdenum**, for instance, is rendered passive by treatment with hydrochloric acid, whilst the activity is restored by treatment with caustic alkali.[2] If passivity is due to the presence of an obstructive oxide film, there is no difficulty in explaining this; the best-known oxide of molybdenum is readily soluble in alkalis forming stable molybdates, whilst it has but feeble basic properties and is only with difficulty dissolved by acids.

Valve Action. In all the metals so far considered the presence of an oxide film or oxygen film does not prevent the passage of electrons across it; and, consequently, the discharge of anions, with the evolution of oxygen gas, can continue even after the anode has become passive. It is evident that if a film exists upon an anode which is an electrical non-conductor, electrodic reactions of that character must cease also. In the case of a polarized aluminium anode this appears to be the case.

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[1] E. K. Rideal, *Trans. Faraday Soc.* **9** (1914), 281.

[2] W. Muthmann and F. Fraunberger, *Sitzungsber. Bayer. Akad.* **34** (1904), 217.

If an electrolytic cell be made up with an aluminium cathode and a platinum anode immersed in dilute sulphuric acid, and an E.M.F. be applied, current passes through the cell quite easily; but, if the E.M.F. now be reversed, so that the aluminium becomes the anode, the current quickly drops and finally ceases to flow altogether. Thus an aluminium electrode acts as a "valve"; it allows current to flow in one direction, but not in the other.

Our knowledge of the causes of valve action is largely due to the work of Schulze.[1] It is well known that a very thin oxide film always exists on the surface of aluminium which has been exposed to the air; the film is normally so thin as to be invisible, but it is the existence of this compact and tenacious layer that allows aluminium—a highly reactive metal—to remain bright and apparently unaffected by the atmosphere. The film is a rather bad conductor of electricity; it is well known that it is rather difficult to make a good electrical contact on an aluminium surface. Nevertheless, owing to the thinness of the film, it does not normally insulate the aluminium, and—as has been stated above—an aluminium plate can be successfully used as a cathode in an electrolytic cell. If, however, aluminium is used as the material for the anode, the case is different, since the effect of the anodic reaction is to make the film thicker. The film is, even at the commencement, sufficient to prevent aluminium from passing into the ionic state; in other words, aluminium is from the commencement passive. As in the case of passive iron, the only possible anodic reactions involve the discharge of anions, leading to the formation of oxygen, and an accumulation of oxygen soon occurs at the surface. It is probable that at first some few of the ions burst through the original protective film, thus making it porous, and allowing the oxygen gas to attack the metal below. As a result, the thin, compact, invisible film of oxide soon becomes converted to a very much thicker layer of porous aluminium oxide; the thickness is indeed often sufficiently great to make a visible change in the appearance of the surface, which begins to show the interference colours characteristic of oxide-films.[1]

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[1] G. Schulze, *Trans. Faraday Soc.* **9** (1914), 266; *Ann. Phys.* **21** (1906), 929; **22** (1907), 543. Another view of valve-action is presented by A. Smits, *Proc. Amst. Acad.* **22** (1920), 876.

Very soon the bottoms of the pores become filled with oxygen gas, and we thus get a layer of gas next to the aluminium; it is this layer of gas which causes the effective electrical insulation of the whole anode. The current, therefore, diminishes and finally ceases to flow altogether, apart from a small leakage current which depends on the E.M.F. applied to the cell. If the E.M.F. applied to the cell containing sulphuric acid is raised to about 25 volts, this leakage becomes very appreciable, and is accompanied by numerous small sparks at the aluminium surface, which presumably indicate the piercing of the film in different places by anions or electrons. If the E.M.F. is raised above 25 volts, the insulating film breaks down altogether, and a large current flows through the cell; in other words the "maximum voltage" which the film can withstand in a sulphuric acid solution is 25 volts.

The magnitude of the leakage current which passes at any given potential (below the maximum voltage) depends both on the temperature and the composition of the bath. It is much greater at high temperatures than at low ones. If a small amount of chloride is added to the sulphuric acid, the leakage current is greatly increased.[2] The leakage is much less in a pure phosphate bath than in a sulphuric acid bath, but the addition of quite small amounts of sulphates or chlorides to the phosphate bath increases the leakage in a most notable degree.[3]

The maximum voltage which can be withstood before a breakdown of the film occurs also varies very greatly with the nature of the bath; whilst in sulphuric acid, the film breaks down at 25 volts, in a borate bath 500 volts must be applied before the film gives way. It is noteworthy that the maximum voltage withstood is generally greater in dilute solutions—in which the anions are scarce—than in concentrated solutions, although exceptions to this rule are known.

The following table gives the maximum voltages attained in various baths by aluminium, and also by tantalum,[4] niobium,[5] magnesium,[6] antimony,[6] bismuth,[6] zirconium,[7] zinc,[8] and cadmium[8] —other metals which show valve-action under certain conditions.

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[1] C. I. Zimmermann, *Trans. Amer. Electrochem. Soc.* **5** (1904), 147.

[2] W. W. Taylor and J. K. H. Inglis, *Phil. Mag.* **5** (1903), 301.

[3] G. E. Bairsto and R. Mercer, *Trans. Faraday Soc.* **7** (1911), 1; W. R. Mott, *Electrochem. Ind.* **2** (1904), 352.

[4] G. Schulze, *Ann. Phys.* **23** (1907), 226; **65** (1921), 223.

[5] G. Schulze, *Ann. Phys.* **25** (1908), 775.

[6] G. Schulze, *Ann. Phys.* **24** (1907), 43.

[7] L. H. Walter, *Electrician*, **71** (1913), 1057.

[8] G. Schulze, *Ann. Phys.* **26** (1908), 372.

Aluminium.	Volts.	**Tantalum.**	Volts.	**Niobium.**	Volts.
$(NH_4)_2HBO_3$	500	K_2CO_3 (v. dil.)	650	HCl	300
H_3AsO_4	450	K_2CO_3 (less dil.)	250	$(NH_4)_2HPO_4$ (0·1%)	530
$(NH_4)_2HPO_4$	360	H_2SO_4 (v. dil.)	430	$(NH_4)_2HPO_4$ (10%)	210
$(NH_4)_2CO_3$	260	HCl (dilute)	210		
H_2SO_4	25	KOH (conc.)	70	**Zirconium.**	
		KOH (v. dil.)	450	H_2SO_4 (3%)	165
		H_3AsO_4 (v. dil.)	470	Lithium citrate	125
Antimony.		**Bismuth.**		**Magnesium.**	
KOH	500	KOH	500	KOH	75
KCl (v. dil.)	over 700	KCl (v. dil.)	15	K_2CO_3 (conc.)	120
HCl	250	HCl	10	$(NH_4)_2HPO_4$ containing NH_3	350
HNO_3	0	HNO_3	0	Most other electrolytes	No valve-action
K_2CO_3	500	K_2CO_3	300		
H_2SO_4 (dil.)	220	H_2SO_4 (dil.)	300		
				Zinc.	
				K_2CO_3 (10%)	83
				Cadmium.	
				K_2CO_3 (10%)	31

With regard to the valve-action of metals other than aluminium, it will be noticed that the tantalum film can stand, in many cases, a higher potential before breaking down than can the film formed upon aluminium. Tantalum, antimony and bismuth show valve-action towards most solutions, although not to all; for instance, a tantalum electrode exhibits no valve-action when immersed in a solution containing a fluoride. Magnesium, zinc and cadmium only exhibit valve-action under exceptional conditions.

If a source of alternating E.M.F. is joined through the cell

Al (Covered with film)	Solution of Phosphate or Borate	Pt

it is found that the current passes freely during the half-period when the aluminium is the cathode, but that—assuming that a suitable film has been "formed" on the aluminium electrode—practically no current passes when the aluminium is the anode.

In other words, the alternating E.M.F. sends a unidirectional current through the cell, which is therefore said to exert a "rectifying effect" on the alternating current.

The reason why no current passes when the aluminium is the anode, will be readily understood, but it may appear strange at first that the insulating film should not equally well prevent the passage of current in the opposite direction. It must, however, be remembered that the effective insulator is a film of gas. Experiments on the conductivity of electricity through gases have taught us that, in general, when electricity passes across a gas-space from one piece of metal to another, it does so almost entirely in one direction, free electrons being given off from the surface of the negative electrode. In a rectifying cell fitted with one aluminium electrode, the aluminium of the electrode contains free electrons, and, during the half-period when the aluminium is a cathode, the electrons pass across the gas-film quite readily. When, however, the aluminium becomes an anode, the current ceases, for the aqueous solution on the other side of the film contains no free electrons, and the discharge of the borate or phosphate anions can apparently only occur when they penetrate to within an extremely small distance from the metal of the electrode. This view of the case is supported by the fact that if a piece of platinum foil is brought close up against the immersed portion of an anodically polarized aluminium electrode, so that we have a metallic surface on each side of the gas-film, sparking occurs freely and the potential difference at the aluminium surface sinks to a few volts.[1]

Rectification is only met with in any marked degree at electrodes where a gas-film is believed to exist. A silver electrode, when used as an anode in a solution of potassium bromide, becomes covered with a non-conducting film of silver bromide, which causes the current flowing to become extremely small. But such an arrangement is not an effective rectifier for an alternating current, because there is no gas-film present.[2]

It is of interest to note here the attempts made to employ "electrical valves" commercially in the "rectification" of an alternating current. It would be highly convenient, in industry, to be able to use the E.M.F. provided by an alternating dynamo to charge accumulators. The commonest form of "valve" consists of a plate of aluminium and a plate of carbon immersed in a solution of a phosphate. Four valves of this character can be joined to the source of alternating current X,Y in the manner shown in Fig.

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[1] G. Schulze, *Ann. Phys.* **22** (1907), 555. Compare K. E. Guthe, *Phys. Rev.* **15** (1902), 327.

[2] G. Schulze, *Ann. Phys.* **26** (1908), 372.

88 (the relative position of the aluminium plates, Al, and the carbon plates, C, should be noted); the accumulators to be charged are connected to the terminals P and N, the positive plate of the end accumulator being joined to P. Through each valve-cell, the electron-stream can pass only in one direction, namely that shown by the arrow. Consequently, no matter whether—at any given moment—the side X of the source of alternating current happens to be positive or negative, the terminal P is invariably positive and the terminal N is invariably negative. The charging of the accumulators, therefore, proceeds continuously, irrespective of the direction of the current as sent out from X or Y.

In spite of the convenience of such an arrangement, the aluminium rectifier has not met with much success. The film on the electrode is liable to disappear rather quickly when the current is turned off; moreover, the leakage of current which occurs during the "anodic" half-periods is usually high enough to render the rectifier an inefficient machine; the leakage is—as has been pointed out—greatly increased by the presence of impurities in the solution. The use of other metals in rectifiers has also been considered, but, up to the present date, the practical difficulties do not appear to have been overcome entirely.[1]

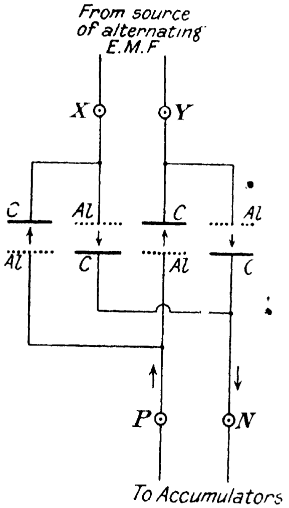

FIG. 88.—Connection of Valves in the Rectification of an Alternating Current.

It is impossible to determine directly the normal electrode potential of any metal, towards a solution in which valve-action occurs; the ordinary method of obtaining a balance with a potentiometer will clearly fail, since the current can only be made to pass in one direction. In the case of aluminium, the formation of the tenacious oxide-film may be avoided by amalgamating the surface with mercury; the true equilibrium potential of oxygen-free amalgamated aluminium is about −1·3 volts, and upon such measurements our knowledge of the value for the normal electrode potential of aluminium is founded. On the other hand, ordinary oxide-coated aluminium never shows a potential lower than about $-0{\cdot}3$ volts and behaves—in actual practice—as a comparatively "noble" material.[1]

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[1] See G. Schulze, *Zeitsch. Elektrochem.* **14** (1908), 303; C. I. Zimmermann, *Trans. Amer. Electrochem. Soc.* **7** (1905), 309; C. F. Burgess and C. Hambuechen, *Trans. Amer. Electrochem. Soc.* **1** (1902), 147 (and discussion on p. 162).

In the case of tantalum, it is possible to determine the potential in a fluoride bath, in which valve-action does not occur.[2]

Classification of Metals according to their Anodic Behaviour. It is possible to classify metals according to the behaviour which they commonly show when used as the material for the anode of an electrolytic cell; it is interesting to note that the classification corresponds—on the whole—with the arrangement of the metals in the form of the periodic table employed in this book.

Class (1). Metals which constitute normal soluble anodes: Copper, silver, zinc, cadmium, mercury, tin and lead. All these metals have perfectly definite equilibrium electrode potentials, which are practically independent of the past history of the electrode employed.

It is interesting to observe that all these metals belong to the "B" groups—occurring on the right-hand side of the periodic table.

Class (2). Metals which can function as soluble anodes at low current densities but which readily become "passive": Iron, nickel, cobalt, chromium, molybdenum, tungsten. A metal of this class has a definite equilibrium potential when in the "active state"; but after anodic polarization at a current density beyond a certain limiting value, it functions as an "unattackable electrode," and the value of the potential is then determined mainly by the amount of oxygen in the electrode, and by the presence—or absence—of oxidizing agents in the solution surrounding the electrode. Thus the potential at an electrode composed of any of these metals depends very much on the "past history" of the electrode.

It is possible that platinum and iridium should be classified with the "passifiable" metals, although the limiting current density in these cases is practically nil, and the metals are almost unattackable under all circumstances.

It is to be noted that most of the metals showing "passivity" belong to the "transition elements" of the periodic table or to neighbouring Group VIA.

Class (3). Metals which show valve-action: Aluminium, zirconium, niobium, tantalum, antimony and bismuth. Such metals cannot—in the ordinary way—function as anodes, and the potential at the electrode surface depends entirely on the past history of the electrode. The normal electrode potential has usually to be determined by an indirect method—for instance by the use of an amalgam—or by the employment of some special solution in which valve-action is not displayed.

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[1] J. Heyrovsky, *Trans. Chem. Soc.* **117** (1920), 27.

[2] G. von Hevesy and R. E. Slade, *Zeitsch. Elektrochem.* **18** (1912), **1001**.

Most of these metals occur in Groups IIIA, IVA, VA and VB of the periodic table, although not all the metals of these groups exhibit valve-action.

Class (4). Metals readily attacked by water, which have soluble hydroxides, can scarcely be tested as anodes. The normal electrode potential is determined by indirect methods, for instance by the use of an amalgam. Such metals are sodium, potassium, calcium and barium, all occurring in Groups IA and IIA of the periodic table.

It is necessary to point out, however, that the classification is only a rough one. Most of the metals of class (1) exhibit a species of passivity when used as an anode in a solution containing an anion which forms an insoluble salt with the metal in question; thus a lead anode in a sodium sulphate solution becomes covered with insoluble lead sulphate, and the attack of the anode gradually slows down.

Silver, used as an anode in hydrobromic acid solution, becomes coated after a time with a practically non-conducting layer of silver bromide, and thus exhibits a species of valve-action. Iron, a typical metal of Class (2), merely becomes passive when used as an anode in dilute sulphuric acid, but is said to exhibit valve-action in concentrated sulphuric acid.

Summary. The anodic dissolution of a metal can be regarded as the spontaneous passage of metal into the cationic state, but is probably in part due to the discharge of anions upon the anode, followed by secondary reactions. If the action of the anion on the metal produces a crust of insoluble salt, the attack upon the metal may soon cease. But if the salt produced is soluble, the metal will probably start to pass into solution, at any rate for a time. So long as the principal anion is the chlorine ion, the metal is likely to continue to be attacked quantitatively. But when the principal anion is $(SO_4)''$, or $(NO_3)'$, or, worse still, OH', oxygen or oxide may commence to accumulate at the anode, and if the current density becomes unduly high, may actually interfere with the passage of the metal into solution. The protective film of oxygen or oxide is very thin, probably consisting of a single layer of adsorbed atoms or molecules; it can be regarded as an oxide-film of variable composition, but must not be identified with any of the oxides known to us in the massive state.

Metals like iron are thus rendered passive anodically if the current density exceeds a given critical value; the potential then becomes highly positive, and the metal behaves as a noble material, and does not recommence to dissolve even if the current density is reduced once more below the critical value. However, in general, if the current is shut off and the metal is allowed to rest, it becomes active again after a short time, the potential dropping to its original (negative) value. Oxidizing agents and anodic treatment favour the production and preservation of the passive state, especially at low temperatures, whilst reducing agents and cathodic treatment favour the active condition, especially at high temperatures. In iron the presence of acids favours the active state, whilst alkalis favour the active state; in molybdenum—and other metals with oxides soluble in alkali—the reverse is the case.

Under certain circumstances, an anode may show "periodicity," becoming active and passive alternately. A passive anode usually dissolves only very slowly, but, in the case of chromium, which has a soluble high oxide, the anode dissolves readily if polarized sufficiently strongly.

Iron can also be rendered passive by immersion in concentrated nitric acid (specific gravity above 1·25), but it is probable that the action is really electrochemical. In nitric acid of specific gravity 1·3, contact of active iron with a noble substance like lead or gold renders it passive, whilst contact with a reactive substance like zinc renders passive iron active.

Where the insoluble film produced upon an anode is a non-conductor of electricity, current will cease to flow. A silver anode immersed in potassium bromide becomes covered with silver bromide, which acts as an insulator and prevents the passage of current. An aluminium anode immersed in borax solution, however, becomes covered with a film of gas, probably enclosed in the pores of a layer of aluminium oxide. The gas-film allows the current to pass in one direction, and not in the other. Thus an aluminium electrode on which a skin has been formed anodically has a rectifying action upon an alternating current. Other metals also display a valve-action of this sort (tantalum, bismuth, etc.); the maximum voltage which the metals will stand as anodes, before the film breaks down, is often high (500–700 volts), but the leakage through the film is greatly increased by the presence of certain anions in solution (notably by chlorine ions).

CHAPTER XIII

THE PRECIPITATION OF ONE METAL BY ANOTHER

The Table of Normal Electrode Potentials indicates the tendency of the different metals to pass from the elementary into the ionic condition. The metals placed at the top of the table, which possess positive potentials, are noble elements which show great reluctance to enter into solution. But, as we pass down the table, the potentials diminish and finally become negative; the metals accordingly become highly reactive and readily enter into the ionic state. If we introduce a piece of one metal into the solution of a normally ionized salt of another metal standing far above it in the Potential Series the two metals will generally change places. For instance, if a fragment of metallic zinc is introduced into a solution of copper sulphate, a spongy red-brown precipitate of metallic copper is produced, whilst zinc passes into the solution, by the evaporation of which zinc sulphate can afterwards be recovered. The reaction can be expressed

$$Zn + CuSO_4 = Cu + ZnSO_4,$$

or, in ionic language,

$$Zn + Cu^{\cdot\cdot} = Cu + Zn^{\cdot\cdot}.$$

The reverse reaction does not occur; if metallic copper is introduced into zinc sulphate solution, no change is observed, since zinc does not stand above copper in the table of normal electrode potentials.

Numerous other examples of one metal replacing another can be given. Metallic zinc will throw down lead, copper, mercury, silver or gold from the solution of a soluble salt of any of these metals. Iron will replace copper, silver or gold. Copper will replace mercury, and so on.

When the normal electrode potential of two metals is close together, the question of the replacement of one by the other is less easy to predict. The normal electrode potential of lead (−0·132 volts) differs but little from that of tin (– 0·146 volts); towards solutions containing *normal* concentrations of the respective ions, lead is the more "noble" metal, but it is only necessary to dilute the solution containing the lead salt slightly to shift the potential and render lead the less noble metal. Thus it comes about that on the immersion of metallic tin in a lead salt solution (free from tin), lead is precipitated, but when metallic lead is immersed in a solution of a tin salt (free from lead), metallic tin is precipitated. In both cases, the equilibrium

$$\mathrm{Sn} + \mathrm{Pb}^{\cdot\cdot} = \mathrm{Pb} + \mathrm{Sn}^{\cdot\cdot}$$

is finally set up, when the ratio of the concentration of $\mathrm{Sn}^{\cdot\cdot}$ to $\mathrm{Pb}^{\cdot\cdot}$ in the solution is about 2·98.[1]

Even more interesting is the case of silver and mercury. Here the normal electrode potentials are so close together that it is still rather doubtful which value is higher. Accordingly mercury reacts with a solution of silver nitrate, whilst silver reacts with a solution of mercurous nitrate. But in both cases, the product of the change is not a pure metal, but an amalgam or alloy of silver and mercury; the proportion of silver and mercury in the alloy, in the final state of equilibrium, will be determined by the respective concentrations of silver and mercury ions in the solution.[2]

There are a few exceptions to the rule given above, which in some cases still require a complete interpretation. Iron, when immersed in a solution of stannous chloride, should throw down metallic tin, but under ordinary circumstances this replacement is not observed; it is stated that the presence of stannous chloride actually causes a serious alteration in the electrode potential of iron,[3] but it is not clear why this should be so. Those metals, like aluminium, which are generally covered with an adherent film of oxide also show a somewhat anomalous behaviour, their precipitating power for other metals being much less marked than the position in the Potential Series would lead us to expect.

When the process of the precipitation of one metal by another is carefully watched, it becomes clear that the process is not quite so simple as might at first sight appear. If, for instance, a piece of metallic zinc is suspended by a thread in a solution of lead acetate, the beautiful "lead tree" is produced. Shining fern-like crystals of lead start growing out from the zinc at different places, and continue to grow until the tips of the growth are perhaps an inch or more from the original piece of zinc.

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[1] A. A. Noyes and K. Toabe, *J. Amer. Chem. Soc.* **39** (1917), 1537.

[2] W. Reinders, *Zeitsch. Phys. Chem.* **54** (1906), 609.

[3] N. Bouman, *Rec. Trav. Chim.* **39** (1920), 537.

If the reaction were the simple interchange of zinc and lead atoms expressed by the equation,

$$Pb^{\cdot\cdot} + Zn = Zn^{\cdot\cdot} + Pb,$$

one would expect to find the metallic lead produced just at those points at which the zinc is being dissolved away. Yet actually we find the lead deposited an inch or more away from the surface of the zinc. It seems as though we have to deal with a case of "chemical action at a distance." Evidently the equation just given—although accurately representing the final result of the interchange of metals—does not fully indicate the steps by which the reaction proceeds. If, however, we remember that the conversion of a metallic atom into a metallic ion is an electrical process, a simple explanation of the difficulty suggests itself.

The matter is best demonstrated by the following series of simple experiments. If a plate of zinc and a plate of lead be joined by wires to the two poles of a galvanometer, and are then immersed, without touching one another, in a solution of lead acetate, the deflection of the galvanometer indicates the flow of a continuous current, the zinc plate functioning as the negative pole. The reactions causing this current are analogous to those occurring in the ordinary Daniell cell, and can be written thus:—

At the zinc plate . . . $Zn = Zn^{\cdot\cdot} + 2e$
At the lead plate . . . $Pb^{\cdot\cdot} + 2e = Pb$

The production of fresh crystalline lead upon the lead plate and the eating away of the zinc soon becomes evident to the eye.

If, instead of being joined together by means of external wires, the zinc and lead plates are allowed to touch below the surface of the liquid, the same reactions appear to continue, the zinc being corroded away, whilst fresh crystalline lead grows out from the lead plate (as well as from the zinc plate also). In this case, although the current is not detected on a galvanometer, there is little doubt that a continual stream of electrons continues to pass from the zinc to the lead at the point of contact. We are still dealing with an electric cell, but it is now a short-circuited cell.

Finally, suppose that the lead plate is omitted altogether, a fragment of zinc being immersed alone in a solution of lead acetate. Here, possibly, the first replacement of lead by zinc may consist in the simple chemical interchange of lead and zinc atoms. But, as soon as a minute amount of lead has been produced at any point upon the zinc, it commences to act as the positive plate of the short-circuited cell,

Zn | Lead Acetate solution | Pb.

and the further deposition of lead occurs, not directly upon the surface of the zinc, but upon the lead nucleus which already exists in contact with the zinc. The tendency of electro-deposited lead to form dendritic growths has already been referred to in Chapter XI, and it is not surprising to find the lead growing out from the zinc in the fern-like crystals which constitute the lead tree. And, although it is difficult to demonstrate the fact, it is fairly certain that, along each growing frond of the lead tree, a stream of electrons is flowing, from the direction of the zinc fragment towards the tips of the fronds where growth is proceeding.

If a fragment of metallic zinc is immersed in the solution of a salt of silver, gold or platinum, the precious metal is brought down as a dark sponge which grows out for an appreciable distance from the surface of the zinc. Here again, the formation of short-circuited electric cells must be assumed to account for the phenomenon. In some other cases, however, the electrical character of the reaction is less obvious. For instance, if a clean bright surface of steel is wetted with a solution of copper sulphate, a thin deposit of metallic copper is produced all over the surface, and clinging closely to it. One might, perhaps, account for the production of the deposit on the assumption that the iron and copper atoms along the whole surface change places in a direct manner. But it is generally considered that here also the action is electrical in character. Commercial iron and steel is an alloy containing, besides grains of pure iron, other comparatively "noble" constituents, such as iron carbide; a particle of this kind is able to act as the unattackable pole of the short-circuited cell,

Iron | Copper sulphate | Noble constituent

As soon as the steel is immersed in the copper sulphate solution, the deposition of metallic copper upon the "noble" portions of the surface commences, and the growth of copper extends in all directions over the surface of the iron, until finally the growths from different centres meet one another; when this occurs—the metallic iron being then practically covered over with the copper layer—the reaction slows down and finally ceases.

This method of covering one metal with a thin coating of another is known as the **method of simple immersion.** It is noteworthy that only those metals like copper, which readily appear as a compact layer when deposited on a cathode by means of an externally furnished current, yield anything approaching a satisfactory coating by the method of simple immersion. This affords important support for the view that the deposit of copper formed by simple immersion is, like the lead tree, of an electrical origin, the current being, in both cases, internally generated. Further evidence for the same view is provided by the discovery, due to Lambert,[1] that perfectly pure, uniform iron will not liberate copper from a copper sulphate solution, although the slightest lack of uniformity in the metal is sufficient to allow it to deposit copper. Even if the iron is simply subjected to pressure in an agate mortar, previous to immersion in the copper solution, the potential is altered at the stressed portions, and the short-circuited cell

Stressed Iron | Solution | Unstressed iron

is set up. The current produced involves the deposition of copper on the cathodic areas of the cell.

A little consideration will show that the layer of metal produced by simple immersion will not be so compact or so adherent as that produced by the ordinary electroplating process with an externally provided current. For, in the copper-plating of steel by simple immersion, the deposition of copper begins to slow down as soon as the growths extending from different points commence to approach one another, owing to the fact that the metal below, which is needed to maintain the current, has been largely covered up by the copper; the growths from the different points are therefore unlikely to be pressed together into good mechanical union. The deposit is, consequently, liable to be incoherent, and probably discontinuous. Moreover, it will, of necessity, be thin. Again, during the process of deposition by immersion, the base metal is being dissolved away at the very moment at which the layer of noble metal is spreading over it; under such circumstances, the deposit cannot be expected to adhere well. Finally, where the current is internally generated, there is no means of controlling the current density, so as to obtain the best conditions for deposition, as is possible in ordinary electroplating.

For this reason, the method of simple immersion has seldom been employed commercially for the production of a protective layer or "plating" upon metallic articles. On the other hand, the precipitation in a spongy form of a comparatively noble metal by another more reactive—and cheaper—metal is considerably used in the "wet" processes of metallurgy. Solutions containing salts of gold or silver are often treated with zinc, or with aluminium—in the form of dust or shavings—the precious metal being reduced to the metallic state. Similarly solutions containing a salt of copper are frequently treated with scrap iron, the copper being usually deposited as a brown spongy mass ("cement copper").

It is noteworthy that when zinc shavings are used to precipitate traces of gold from a dilute solution, the precipitation is greatly facilitated if the zinc is first immersed in a comparatively concentrated solution of a lead salt. Metallic lead is deposited upon the zinc, and afterwards forms the cathodic element of the short-circuited cell

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[1] B. Lambert, *Trans. Chem. Soc.* **101** (1912), 2056; **107** (1915), 218.

Zinc	Dilute solution of gold compound	Lead

Summary. In general, any metal, when immersed in the normally ionized salt solution of a second metal which stands well above it in the Potential Series, will cause the deposition of the second metal in the elementary state. The character of the deposit obtained by such a process points to the replacement having been electro-chemical in character, due to the production of short-circuited cells or "couples."

The method of obtaining a metallic coat by "simple immersion" constitutes an alternative to ordinary electroplating, but, since the deposit usually lacks cohesion and is very thin, the method is only used in a very few cases. On the other hand, the precipitation of a valuable noble metal (such as gold, silver or copper) by a more reactive one (zinc, aluminium, iron) is largely used in metallurgy.

CHAPTER XIV

THE CORROSION OF METALS

Corrosion by Acids.[1] In the last chapter the precipitation of one metal by another more reactive metal was considered in a general manner. One especially important case has now to be studied in detail—that in which the "metal" displaced from the ionic condition is hydrogen.

Generally speaking, all the metals which occur below hydrogen in the Potential Series are capable of causing an evolution of hydrogen gas when introduced under suitable conditions into the dilute solution of a "strong" (i.e. a largely ionized) acid. The velocity of the reaction often varies to a very marked extent with the purity of the metal. Pure zinc, for instance, is almost unattacked by pure dilute sulphuric acid, but, if the zinc be touched with a copper rod below the surface of the acid, dissolution of the zinc at once commences with copious evolution of hydrogen gas. It is noteworthy that the hydrogen bubbles are actually evolved from the copper rod, not from the zinc itself, although it is the zinc—and not the copper—which is passing into solution. This fact at once suggests that a short-circuited cell of the type,

Zinc | Dilute Sulphuric Acid | Copper

has been produced, and that the production of such a cell is the cause of the rapid attack.

Instead of touching the zinc with a copper rod, the violent reaction of pure zinc with the acid can be brought about in another way, namely by adding a trace of copper sulphate to the acid. At once metallic copper is deposited on the surface of the zinc; short-circuited cells (or "couples") of the type just described are formed all over the surface, and the rate of attack by the acid becomes very violent.

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[1] Many apparent inconsistencies in the behaviour of metals towards acids are explained by W. D. Richardson, *Trans. Amer. Electrochem. Soc.* 38 (1920), 245.

If the zinc is impure, the "couples" may be formed upon the surface even without any addition of copper sulphate or similar salt to the solution. If the zinc contains a mere trace of a comparatively noble metal, such as copper, nickel, gold or platinum, the rate of attack by acid is notably increased. The attack of acid upon slightly impure zinc is often not very rapid when the metal is first immersed in the acid, because the small amount of impurity may exist in solid solution in the zinc and will not therefore constitute the cathodic element of a corrosion couple at the moment of immersion. The slow action, however, brings a certain amount of the noble metal into solution, and it is then reprecipitated, as a separate phase, upon the surface of the metallic zinc. As soon as this occurs, the couple

Zinc | Acid | Noble metal

appears, and the attack by the acid becomes very much quicker. The period of comparatively slow attack which is noticed when first the zinc is immersed in the acid is commonly referred to as the "**period of induction.**"[1]

It is noteworthy that the presence of lead, cadmium and arsenic in zinc adds very little—if at all—to the rate of attack by acids; this is probably connected with the high value of the over-potential of hydrogen evolution upon these metals, which is, at low temperatures, almost equal to the E.M.F. generated by the couple.

The presence of impurities has a similar effect in the case of other metals. Cast iron—which contains crystals of iron carbide or flakes of graphite embedded in it—is attacked more readily by dilute acids than the purer forms of iron.

When we come to metals like tin or lead, which occur close to hydrogen in the Potential Series, we find much less readiness to dissolve in dilute acids. Tin, for instance, is very little attacked by hydrochloric acid at ordinary temperatures, but the action is aided by contact with a metal like copper, or by warming the liquid. It is probable that the slow reaction of tin with hydrochloric acid at low temperatures is connected with the high "overpotential" of the metal. The value of the overpotential diminishes as the temperature rises.

The metals—such as copper or silver—which stand above hydrogen in the Potential Series cannot in any case yield hydrogen *as a gas* by interaction with dilute acids. It is, however, a mistake to suppose that they cannot displace hydrogen at all. If a copper and platinum rod be brought into contact in a dilute acid, so as to produce the short-circuited cell

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[1] The effects of impurities upon the action of acids on zinc are studied by M. Centnerszwer and J. Sachs, *Zeitsch. Phys. Chem.* **87** (1914), 692; **89** (1914), 213; M. Centnerszwer, *Zeitsch. Phys. Chem.* **92** (1918), 563. But these investigators take a view rather different from that suggested above.

Copper | Dilute Acid | Platinum,

the copper commences, momentarily, to enter into solution, and a small amount of hydrogen is produced at the platinum surface. But long before the concentration of hydrogen on the platinum reaches the saturation value, the P.D. at the platinum surface becomes equal to that at the copper surface, and the current therefore ceases. If, however, an oxidizing agent, such as hydrogen peroxide or sodium hypochlorite is added to the acid, which will continuously remove this hydrogen as fast as it is formed, the entry of the copper into the solution proceeds continuously.[1] As a matter of fact, it is found that both copper and silver are dissolved readily by dilute sulphuric acid containing peroxide.[2] Here, there is, of course, no evolution of hydrogen in bubbles; the hydrogen is oxidized to water as fast as it is produced. With ordinary copper or silver, contact with platinum is not necessary, the surface of the metal being usually sufficiently variable in composition to allow the formation of the necessary couples.

In some cases, the acid itself may act as the oxidizing agent. Hot concentrated sulphuric acid is, for instance, a powerful oxidizing agent, and is capable of attacking copper, mercury or silver; sulphur dioxide is evolved, and a sulphate of the metal in question may be recovered from the solution by evaporation. The reaction should probably be regarded as electrochemical, the sulphur dioxide being produced by the interaction of the hydrogen and the sulphuric acid.

$$H_2SO_4 + 2H = 2H_2O + SO_2.$$

Another powerful oxidizer is nitric acid, which displays oxidizing properties even when quite dilute and at ordinary temperatures. Nitric acid attacks practically all metals except iridium, gold and platinum, which stand at the "noble" end of the Potential Series. In only exceptional cases is hydrogen evolved in gaseous form; more often the hydrogen produced reacts with a further quantity of nitric acid to give one of the other substances shown in the following list:—

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[1] The existence of a current accompanying the attack of copper in contact with platinum by acid—or even by ordinary tapwater—containing a trace of hypochlorite can easily be demonstrated. See E. K. Rideal and U. R. Evans, *Analyst*, **38** (1913), 353.

[2] O. P. Watts and N. D. Whipple, *Trans. Amer. Electrochem. Soc.* **32** (1917), 257.

Nitric peroxide	NO_2
Nitrous acid	HNO_2
Nitric oxide	NO
Nitrous oxide	N_2O
Nitrogen	N_2
Hydroxylamine	NH_2OH
Ammonia	NH_3
Hydrogen	H_2

Most of these substances are gaseous and are evolved in bubbles; but ammonia and hydroxylamine remain in solution as soluble nitrates.

The substances standing near the bottom of the list, which are rich in hydrogen, are formed when a reactive metal (which would produce the primary hydrogen under considerable pressure) is introduced into the acid. Thus magnesium and zinc produce a good deal of ammonia, and the first-mentioned metal, when dissolving in dilute nitric acid, actually causes the evolution of a certain amount of unchanged hydrogen. On the other hand, the more noble metals, like copper and silver, give rise to the more highly oxidized substances standing near the top of the list. But the character of the substances produced depends largely on the concentration of the nitric acid; dilute solutions favour the production of a substance comparatively low on the list, whilst concentrated acid naturally gives rise to a more highly oxidized body. Iron, for instance, yields mainly nitric oxide with dilute acid; but with concentrated acid, there is also nitrogen peroxide in the gases evolved.

Certain metals—such as iron and nickel—quickly become passive when acted on by concentrated nitric acid. It is quite to be expected that passivity will be brought about more quickly if a "noble" substance (e.g. a platinum wire) is brought in contact with the iron; this has been shown to be the case. Nor is it surprising to find that cast iron, which contains noble constituents, becomes passive in nitric acid more readily than pure iron; consequently just that form of iron which is most readily attacked by dilute sulphuric acid is comparatively little attacked by nitric acid.[1] These facts, although not conclusive, appear to confirm the view that the action of nitric acid upon metals is, like that of non-oxidizing acids, electrochemical in character, depending on the formation of a "couple," or short-circuited electric cell.

The action of nitric acid does, however, seem to be more complex than that of most other corrosive agents. The corrosion of copper by nitric acid, for instance, appears to be catalytically accelerated by the nitrous acid which is produced in the reaction. When a fragment of copper is placed in nitric acid, the action is slow at first, and then becomes much quicker as nitrous acid accumulates in the solution. Nitric acid which is entirely free from nitrous acid has practically no action on copper, and if a little urea—a substance which destroys nitrous acid—is added to the liquid, copper can remain in nitric acid for some considerable time without being dissolved.[1]

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[1] Contrast pointed out by W. D. Richardson, *Trans. Amer. Inst. Chem. Eng.* 13 (1920), i. 265.

The metals, platinum and gold, which are too noble to be attacked by nitric acid, are nevertheless brought into solution as chlorides by the action of "aqua regia," a mixture of concentrated nitric and hydrochloric acids.

Arranging the commoner metals in the order of their normal electrode potentials, we can summarize the action of acids upon them as follows:—

Gold Platinum	Attacked by aqua regia only.
Silver Mercury Copper	Attacked by oxidizing acids (nitric or hot concentrated sulphuric).
(Position of Hydrogen here.)	
Tin Lead	Attacked by warm concentrated hydrochloric acid.
Iron Cadmium Zinc Aluminium Magnesium	Attacked by dilute sulphuric acid or hydrochloric acid.
Calcium Sodium Potassium	Attacked even by water.

Corrosion of Metals by Neutral Salts. Since hydrogen ions exist, to a small extent, even in a neutral solution, it might easily be expected that the more reactive metals would displace hydrogen when brought into the solution of a neutral salt or even into pure water. In some cases, this is found to be the case; it is well known, for example, that the metals sodium and potassium are violently attacked by water, hydrogen gas being evolved in profusion. But, in any instance, the displacement of hydrogen from an originally neutral solution must leave the liquid alkaline, and, if the hydroxide of the metal attacked happens to be sparingly soluble in the liquid employed, a layer of the hydroxide will tend to collect on the surface of the metal and will often protect it from further corrosion. The exact nature of the factors which determine whether a film of oxide or hydroxide will "protect" the metal or not, have never properly been investigated. It is noteworthy that the presence of chlorides—although it does not, in general, prevent the formation of an insoluble hydroxide—often causes the hydroxide to appear in a non-compact, comparatively voluminous form which does not protect the underlying metal from further attack. The behaviour of chlorides in preventing the passivation of metals by anodic action is, of course, merely another manifestation of the same phenomenon. It is probable that the action of chlorides may be explained by a consideration of the interfacial tension of the materials involved, and should be regarded as due to the "loosening" or "partial peptization" of the oxide-film.[1]

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[1] V. H. Veley, *Proc. Roy. Soc.* **46** (1889), 216; *J. Soc. Chem. Ind.* **10** (1891), 204.

In general, we can only expect a rapid and continuous attack of a metal by a salt solution in cases where the hydroxide is freely soluble in the liquid in question. In the case of sodium, potassium, calcium and barium, the hydroxides are freely soluble, and the metals will continue to evolve hydrogen with violence from an aqueous solution for an indefinite period. The hydroxide of magnesium is soluble in ammonium chloride, and thus metallic magnesium will evolve hydrogen readily from ammonium chloride solution. On the other hand, the hydroxide of aluminium is insoluble in ammonium chloride, and, consequently, ammonium chloride has a slower action upon metallic aluminium and the rate of attack slows down as the hydroxide accumulates. The majority of the metals above aluminium in the Potential Series have sparingly soluble hydroxides, and are only slowly attacked by neutral solutions.

Corrosion of Metals by Alkalis. The same general considerations apply to the question of the corrosion of metals by alkalis.

The metals, aluminium and zinc, whose oxides are amphoteric, are readily attacked by a solution of sodium hydroxide, soluble aluminates or zincates being formed. Hydrogen is evolved in profusion, in spite of the low concentration of hydrogen ions in alkaline solutions. Magnesium, which forms no soluble compounds analogous to the aluminates, is comparatively unattacked by alkaline solutions. Iron becomes passive in dilute alkaline solutions, but is slowly attacked by hot concentrated caustic soda; part of the hydrogen produced penetrates into the iron, causing inter-granular brittleness.

Corrosion by Cyanides. It has been explained in Chapter

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[1] U. R. Evans, *Trans. Faraday Soc.* 18 (1922), 3.

IX that the P.D. between a given metal and a solution in which that metal does not normally occur as a cation, is very different from the P.D. shown by the same metal in a solution of its sulphate or chloride. Towards cyanide solutions in particular, the P.D. of several metals—like copper, silver and gold—is much lower (less "noble") than towards ordinary salt solutions. It is not surprising that these metals—which are unattacked by ordinary acids—are readily dissolved by a potassium cyanide solution in the presence of air, oxygen being needed—at least in the case of gold—to combine with the hydrogen produced in the reaction.

Corrosion by "Water." Far more important to the ordinary man than the rapid corrosion of metals by acids or alkalis is the slow change caused by the action of ordinary water upon the common industrial metals and alloys, such as iron, lead, brass and bronze. The corrosion of these materials will call for further study in the later volumes of this book, when the metal or alloy in question is being described, but a few general observations must be made at this point. The water used for industrial and domestic purposes, generally derived from rivers or from wells, is very different from the pure distilled water of the laboratory. It contains many substances in solution, mostly derived from the rocks through which the water has passed. Most of these are comparatively inert substances such as calcium bicarbonate, calcium sulphate, magnesium sulphate, sodium chloride and silica. Sometimes the water contains carbon dioxide, and has an acid reaction; sometimes, it contains sodium carbonate and is weakly alkaline. But, far the most important substance present in the water—from the point of view of corrosion—is dissolved oxygen. The amount of oxygen in a water supply depends very much on the method of storage and conveyance, and also on the organic contamination of the supply, being naturally least in polluted waters. But it is practically never wholly absent, and can, generally speaking, be looked upon as the essential factor in determining corrosion.

The common metals, iron and lead, although capable of liberating hydrogen in gaseous form from distinctly acid liquids, rarely, if ever, cause an evolution of hydrogen in gaseous form from the ordinary industrial water, in which the hydrion concentration is necessarily low. Generally speaking, therefore, they are but little attacked by waters which have been freed from dissolved oxygen. On the other hand, where oxygen exists in the water, it acts as an oxidizing depolarizer, removing the hydrogen as soon as it is formed, and causing the corrosion to proceed apace. It has been proved that the action of dissolved oxygen upon the hydrogen produced at the cathode of an electrolytic cell produces not only water but also hydrogen peroxide.[1] It is not surprising, therefore, to find that hydrogen peroxide is sometimes found upon the surface of a metal during the process of corrosion.[2] The presence of hydrogen peroxide has, indeed, been looked upon by some chemists as an essential condition for corrosion; but such a view is almost certainly wrong; the presence of hydrogen peroxide is the *effect* of corrosion—not the cause.

There are many indications that the mechanism of corrosion is really electrochemical. It has been shown that—whilst ordinary commercial iron rusts quickly if exposed to the combined influence of water and oxygen—iron that is absolutely pure and uniform is unattacked under the same conditions.[3] The preparation of the pure uniform iron is, however, a most laborious process. The presence of any "noble" substance which is a conductor of electricity always causes corrosion at the point of contact. The accidental inclusion in the iron of the merest trace of platinum, caused by the use of platinum dishes in the preparation of the material, is sufficient to cause the iron to rust.

For ordinary purposes, it is useless to aim at the production of a material so pure and uniform as to be free from corrosion. In almost any commercial metal, there is sufficient impurity to set up a corrosion couple, and the rate of corrosion is determined by the supply of oxygen in the water rather than by the purity of the sample; it is not always true that a highly impure sample of commercial metal will be corroded more quickly than a moderately pure sample of the same metal. But whilst the purity of the metal—as revealed by analysis—is practically no guide to its behaviour towards corrosive agencies, the condition of the surface is important. Metal articles which have been worked superficially or highly polished are usually covered with a smooth skin of practically amorphous matter of very uniform composition, and this uniform skin undoubtedly plays a great part in preventing the inception of corrosion.[4]

Numerous examples have been recorded by engineers of the acceleration of corrosion by contact with a noble substance. In one case, an iron pipe buried in the ground passed at a certain place through a cinder filling; where the cinder came in contact with the iron, very marked corrosion was found to have occurred, the couple

Iron | Ground-water | Cinder

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[1] F. Richarz and C. Lonnes, *Zeitsch. Phys. Chem.* **20** (1896), 145.

[2] M. Kernbaum, *Comptes Rend.* **152** (1911), 1668.

[3] B. Lambert and J. C. Thomson, *Trans. Chem. Soc.* **97** (1910), 2426; B. Lambert, *Trans. Chem. Soc.* **101** (1912), 2056; **107** (1915), 218.

[4] H. W. Brownsdon, *J. Soc. Chem. Ind.* **39** (1920), 432R.

being set up.[1] Again, where the steel hull of a ship is in contact with a bronze casting, special corrosion of the steel practically always occurs, unless some precaution is taken to prevent it.[2]

Nor is the presence of a second distinct material needed to produce the type of couple which leads to especially rapid corrosion. If a metal is strained mechanically, the P.D. at the surface of the strained portion—possibly owing to the presence of amorphous metal—is slightly different from that at the surface of the unstrained portion. Consequently, a couple of the type

Strained Metal	Water	Unstrained Metal

is formed, and corrosion sets in. As a result, corrosion is often found in pieces of metal which have been subjected to strain, and which have not been properly annealed afterwards. It has been found, for instance, in plates in which rivet holes have been punched, that corrosion often occurs around the holes, owing to the strain set up.[3] Aluminium is particularly liable to a most destructive type of corrosion caused by local straining, and all aluminium articles should be carefully annealed before being put into use.[4]

Although the presence of acidity in the water is not—in general—a necessary condition of corrosion, yet, if the electrochemical view of corrosion sketched above be accepted, it is clear that the concentration of hydrion in a water is a very important factor in determining the rate at which metals will be attacked by it. Waters containing carbon dioxide cause iron to rust considerably more quickly than those free from acidic substances. Indeed, at one time, the presence of carbon dioxide was thought to be essential if the corrosion of iron was to occur: this view is now known to be wrong, but the presence of carbon dioxide is often a very important contributing cause of corrosion.[5] Magnesium chloride, a salt which often occurs in the waters of desert regions, confers, owing to hydrolysis, a distinct acid reaction upon the water. Unless this acidity is neutralized, waters containing magnesium chloride have a marked corrosive action upon iron pipes.

Many other constituents of ordinary "tap-water" have a considerable influence upon the rate of corrosion. In general, small amounts of dissolved salts, by increasing the conductivity of the water, tend to favour corrosion. Not infrequently, however, the presence of an excessive quantity of salts is found to reduce the rate of corrosion—possibly because it reduces the solubility of oxygen in the water.[1] In the case of iron and steel, the presence of small quantities of chlorides is favourable to corrosion because the chlorides prevent any possibility of the iron becoming passive. Generally speaking, seawater is much more corrosive than fresh water.

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[1] W. B. Schulte, *Trans. Amer. Electrochem. Soc.* **22** (1912), 209.

[2] F. Lyon, *Engineer,* **115** (1913), 451.

[3] C. F. Burgess, *Trans. Amer. Electrochem. Soc.* **13** (1908), 17; W. H. Walker and C. Dill, *Trans. Amer. Electrochem. Soc.* **11** (1907), 153.

E. Heyn and O. Bauer, *Mitt. Kgl. Mat. Prüfungsamt,* **29** (1911), 2.

[5] W. A. Tilden, *Trans. Chem. Soc.* **93** (1908), 1356; W. H. Walker, *J. Amer. Chem. Soc.* **29** (1907), 1251; E. Heyn and O. Bauer, *Mitt. Kgl. Mat. Prüfungsamt,* **26** (1908), 1.

It is well known that "hard" waters are generally less corrosive than "soft" ones. The former usually contain the soluble but rather unstable salt, calcium bicarbonate ($CaH_2(CO_3)_2$); this is liable to decompose at the surface of the metal and a solid scale of insoluble calcium carbonate is produced over the surface, which is thus shielded from further corrosion. Not infrequently, the "corrosion-product" itself protects the surface of the metal. The carbonate and sulphate of lead are both sparingly soluble; and when ordinary hard water, containing plenty of carbonates and sulphates, passes through a lead pipe, the metal soon becomes covered with an insoluble coating which prevents further action. On the other hand, if the water be a "soft" one, and especially if it contains nitrites or organic acids, it will dissolve an appreciable quantity of lead; and, if the water be afterwards used for drinking purposes, lead poisoning may result.

Many metals such as aluminium and zinc appear to be invariably covered with a very thin transparent film of closely adherent oxide, which renders these metals much more resistant towards ordinary corrosion than might be expected from their position in the Potential Series.

Protection of Metals against Corrosion. In most cases, where a piece of metal has to be exposed to the combined influences of water and oxygen, it is advisable to take some steps to prevent corrosion. Occasionally—for instance, where water is required for a boiler—it may be possible to **treat the water** so as to render it less objectionable. It may be treated with an alkaline substance such as sodium carbonate or lime-water, so as to remove all traces of acidity. Or it may be freed from dissolved oxygen by preliminary heating, or by treatment with valueless scrap iron. Where the boiler is constructed of iron, a chromate is sometimes added to the feed-water, in order to bring the iron to the passive condition.

Except in the case of water for a boiler, however, it is generally necessary to treat the metal instead of treating the water. The most obvious plan is to cover the whole surface of the metal with a layer of some less corrodible material, which may consist of another metal, or a coating of paint or varnish.

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[1] See J. N. Friend and P. C. Barnet, *J. Iron Steel Inst.* **91** (1915), 336, and also J. N. Friend, *Trans. Chem. Soc.* **119** (1921), 932, especially page 937. Friend thinks that the diminished solubility of oxygen cannot be the only factor in causing the diminished rate of corrosion.

Consider first the method of **protection by a skin of a less corrodible metal.** Quite a number of metals are used, under different circumstances, to protect iron or steel objects from corrosion; zinc, nickel, tin, lead, cobalt and copper have all found application for the purpose. So long as the coating of protective metal completely covers the whole surface of the iron, each of these metals is quite effective. But if, owing to the existence of "pin-holes" in the covering, or through the wearing away of the protecting metal, the iron or steel becomes exposed at any point, the case requires further consideration. Suppose, for instance, a covering of tin upon a steel plate is not continuous, but contains numerous pin-holes, and that the surface becomes wetted with water containing oxygen, corrosion couples of the type,

Iron | Water | Tin

are set up. Here iron forms the attackable pole of the cell, since tin stands above iron in the Potential Series. Thus the corrosion of the iron, at the exposed points, is probably more rapid than if the tin covering were absent altogether. The same applies to coverings of copper, nickel, lead and gold, which also have normal electrode potentials more positive than iron. The covering is perfectly satisfactory if it is continuous; but, if the iron is exposed at points, the covering is, in the neighbourhood of these points, useless—or even worse than useless.[1] Some years ago, gold-plated steel nibs were put on the market in America; but it was found that the gold was soon rubbed away at the tip, and the nib then became corroded much quicker than an ordinary unplated nib.[2]

When a covering of zinc is employed, the state of affairs is different. A sheet of galvanized (i.e. zinc-covered) iron may have the iron exposed at various points, and yet comparatively little corrosion of the iron occurs. It is true that the corrosion couples

Zinc | Water | Iron

are set up; but, since zinc stands below iron in the Potential Series, the attackable pole of the cell is the zinc, not the iron. The P.D. at the iron surface is changed in a negative sense by contact with the zinc, and the tendency of the iron to enter the ionic state is consequently diminished. Therefore the mere contact with zinc tends to prevent to some extent the corrosion of iron, even if the iron is exposed in places.[1]

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[1] O. P. Watts and P. L. Deventer, *Trans. Amer. Electrochem. Soc.* **11** (1907), 153.

[2] W. S. Landis, *Trans. Amer. Electrochem. Soc.* **19** (1911), 59.

This brings us naturally to another method which has been used considerably for the prevention of corrosion of iron and steel. Zinc pieces are bolted to different parts of the iron article, but no attempt is made to cover up the surface as a whole. As a result of the corrosion couples set up, it is the zinc which is eaten away, whilst the iron article is protected. The zinc "protectors" have, of course, to be renewed from time to time. The method appears to be quite effective so long as the zinc surface is kept clean and bright. But, if the surface becomes covered with oxide, hydroxide, or some similar insoluble compound, the corrosion of the zinc is interfered with; the current falls off and the protective action upon the iron ceases. On account of this fact, the employment of zinc protectors for iron has tended to pass out of favour.[2]

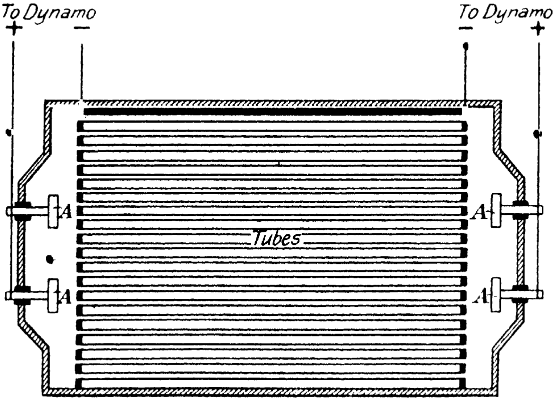

FIG. 89.—Electrolytic Protection of Condenser Tubes (Cumberland System).

There is, however, another method of preventing corrosion which is, in principle, similar to that discussed above, but which dispenses with the use of the zinc protectors.[3] It is employed, to some considerable extent, in the prevention of corrosion of marine condenser tubes, and is said to be very effective. Blocks of cast-iron, A, carefully insulated from the brass tubes, are fixed in the reservoirs with which the condenser tubes communicate (Fig. 89). The condenser tubes and the iron blocks are joined to an electric battery, or to a dynamo, in such a way that the tubes are the cathodes and the iron blocks are the anodes. Since the current is provided from an exterior source, it does not tend to fall off with the time, as in the case of the current generated by means of zinc protectors. The condenser tubes, being cathodically polarized, are to a large extent protected from corrosion.

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[1] According to L. Aitchison, *Trans. Faraday Soc.* **16** (1921), 473, the protective influence of zinc is in practice only slight. At the exposed points the iron is attacked at approximately the same rate as though the zinc were entirely absent.

[2] F. Lyon, *Engineer*, **115** (1913), 451.

[3] E. Cumberland, *J. Inst. Met.* **15** (1916), 192.

The fact that the corrosion of a metallic body is largely prevented when it is made the cathode of an electrolytic cell constitutes additional evidence that corrosion is essentially an electrochemical phenomenon. But it has been shown that—under certain circumstances—the corrosion of a cathode can proceed, to a small extent, even when a considerable current is passing; and this fact is regarded by some chemists as showing that corrosion is not entirely electrochemical in origin, and may proceed by direct chemical attack upon the metal by some substance dissolved in the water.[1]

When one passes to consider the **protection of metal by paint or varnish,** the same sort of considerations apply as in protection by a metallic film. The ideal protective coat would be continuous (that is free from pin-holes), durable, impervious to oxygen and to moisture, and would have no electrical conductivity. Probably these conditions are impossible to realize. It is doubtful, for instance, whether a coat of paint impervious to oxygen would ever "dry." At any rate, in practice, the phenomenon of "iron rusting below the paint" is often met with. The paint vehicle has usually an appreciable electrolytic conductivity, and couples between the more reactive and the more noble portions of the metallic surface, of the type,

Reactive Metal	Paint Vehicle containing oxygen and moisture	Noble Particles in Metal

are freely set up, and corrosion occurs. It appears very likely that even in the absence of oxygen, an unsaturated constituent of the paint film (linoxyn) may absorb hydrogen and thus acts as a depolarizer.

Clearly a vehicle which contains little absorbed moisture, has a low conductivity, and is as nearly as possible impervious to oxygen, will (other things being equal) give the best protection from corrosion.[2]

Some authorities consider that the pigment particles themselves have a very marked effect upon the rate of corrosion.[1] Carbon, for instance, is a conductor of electricity, and might be expected to act as the cathode of the cell.

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[1] G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 128.

[2] See W. C. Slade, *J. Ind. Eng. Chem.* **4** (1912), 189; N. A. Dubois, *J. Ind. Eng. Chem.* **5** (1913), 968. Also J. N. Friend, *Carn. Schol. Mem.* **1** (1913); H. A. Gardner, *J. Franklin Inst.* **179** (1915), 313.

Metal	Paint Vehicle	Carbon

In actual fact, black paint, in which the pigment is lampblack or graphite, has been found to cause corrosion at a very serious rate, and such a paint should be avoided for protective purposes. On the other hand, when lead chromate is used as a pigment upon iron, the rate of corrosion is extremely small, no doubt owing to the passivating influence of chromates upon iron. Basic or alkaline pigments likewise tend to reduce corrosion.

Corrosion through stray Electric Currents. In the neighbourhood of large towns and districts served by electric tramways, another potent cause of the corrosion of metal arises in the "stray currents" which are found passing through the ground. In the ordinary electric tramway the current is, as is well known, delivered by an overhead conductor, but is left to return to the generating station by means of the rails. The majority of the current undoubtedly does return by this route, but a considerable proportion usually penetrates into the ground, and travels along any buried water-pipes or gas-mains which happen to lead in the right direction, afterwards leaving the pipes in question and rejoining the rails nearer to the station. The proportion of the current returning by this indirect path will depend, of course, on the relative resistances of the direct and indirect routes. If the ground is damp and the connections between the rails poor, the amount of "stray currents" will often be considerable. The strength of the stray current passing along one 6-inch pipe in New York was found in the year 1903 to be 70 amperes.[2] Now, if the stray current were to flow back to the station along an entirely metallic path, it could do no possible harm to the pipes or rails which constitute the path. But where the current has to pass across a certain length of damp ground so as to get from one pipe or rail to another, an electrolytic cell of the type

First Pipe (or rail)	Damp Ground	Second Pipe (or rail)

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[1] A rather extreme view of the importance of the pigment material is expressed by E. Liebrich and F. Spitzer, *Zeitsch. Elektrochem.* **18** (1912), 94, **19** (1913), 295, and is criticized by G. Pfleiderer, *Zeitsch. Elektrochem.* **19** (1913), 507, who considers that the conductivity of most pigments is too low and their contact too poor to allow them to act as the cathodic elements of corrosion-couples.

[2] A. A. Knudson, *Trans. Amer. Electrochem. Soc.* **3** (1903), 195.

is set up, and the pipe or rail constituting the anode of the cell usually suffers corrosion. Where the iron is set in cement the slightly alkaline character of the cement is favourable to the iron becoming passive, and the corrosion is usually less serious. Nevertheless cases have occurred in which the steel girders of ferro-concrete buildings have suffered severely as the result of stray current. The lead sheathing of buried telephone cables is also found to become badly corroded owing to the same cause.[1]

There are various methods of protecting buried metals from the effects of stray currents. In certain cases, the metal can be painted, if possible with chromate pigments or pigments of a basic character. Various mixtures containing tarry substances and hydrocarbons are also largely used. It has been proposed in some cases electrically to connect all the buried metal pipes of the whole city to the rails of the tramway systems, so that the stray currents should, in any case, return by a wholly metallic path.[2] Without adopting this rather " heroic " policy, there is little doubt that the disastrous effects of stray currents can be reduced in various ways by precautions exercised by the proprietors of the tramways. It may be remarked that where an alternating current is used for purposes of electric traction, instead of a continuous current, little corrosion is caused.

Character of the Corrosion Product. When a metal is attacked by an acid, a soluble salt is, in general, produced, and little or no solid corrosion product is left on the metal. Where, however, a metal is corroded by a nearly neutral water, insoluble substances are usually found to collect upon the surface of the metal. Consider, for instance, the electrochemical corrosion of commercial zinc in water containing sodium chloride. In the short-circuited cell,

Zinc	Sodium Chloride solution	Noble Impurities

zinc chloride will be formed in solution at the anode, and sodium hydroxide at the cathode. These will diffuse together, and interact, producing a slimy precipitate of zinc hydroxide, or possibly a basic chloride, which will probably cling to the surface of the zinc.

In the case of iron, there is an additional complication. Ferrous hydroxide, the corrosion product first formed, is perceptibly soluble in water, but it is soon oxidized by the dissolved oxygen present to the far more insoluble ferric hydroxide, which is the essential constituent of ordinary brown rust. The hydroxide is, however, usually mixed with carbonates, and if the iron contains the elements silicon, phosphorus or sulphur, may contain in addition silicates, phosphates or basic sulphates.

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[1] F. Haber and F. Goldschmidt, *Zeitsch. Elektrochem.* **12** (1906), 49 ; M. Girousse, *Comptes Rend.* **157** (1913), 705 ; F. Bergius and P. Krassa, *Zeitsch. Elektrochem.* **15** (1909), 712.

[2] E. K. Rideal, *Trans. Soc. Eng.* **4** (1913), 243.

The character of the corrosion product has a most important influence on the subsequent course of the corrosion. If the product clings closely to the metal, it may form a protective varnish over the surface, and prevent further attack. A very slight variation in the conditions may clearly make a great deal of difference to the protective character of the material. Thus the presence of 1 per cent. of tin in brass causes a considerable decrease in the rate at which the alloy is attacked by sea-water. The reason for this is simply that, when the alloy contains tin, a layer of basic tin salt is quickly formed which adheres to the surface firmly, and constitutes an impermeable varnish.[1]

In this instance, the presence of the corrosion product tends to put a stop to corrosion. There are, however, many cases in which the existence of the corrosion product upon the metal is actually favourable to further attack. Every one knows that when once iron has commenced to rust at a place, it is very difficult to stop the rusting at that point. There are various reasons for this, the first being very simple. If an iron object is exposed to a shower of rain, the rusty parts remain damp long after the rain has stopped, whilst the bright parts quickly dry; hence, further corrosion is likely to take place upon the parts where rust already exists. Moreover, if the rust finally becomes entirely dry, the hydroxide may become converted to the oxide (Fe_2O_3), which is liable to act as the cathode of a corrosion couple, on the next occasion when the iron becomes wetted.

The above two explanations apply in cases in which the iron is allowed periodically to become dry. But rust seems to favour the continuation of corrosion even when the metal is constantly immersed in water. The reason for this appears to be that the rust prevents to a large extent the diffusion of dissolved oxygen to the portions of metal immediately below it. At first sight, it might be thought that corrosion would thereby be retarded, but it must be remembered that the P.D. of iron is itself largely affected by the presence of oxygen. We may, therefore, get corrosion cells of the type,

Iron	Water free from oxygen	Water containing oxygen	Iron

set up. In this case it is the iron below the rust, to which the oxygen has *not* access, which is attacked—a result quite in accordance with the general character of electrochemical action.[1]

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[1] C. H. Desch, *Trans. Faraday Soc.* 11 (1916), 202.

In many of the copper alloys, the existence of basic copper salts in the corrosion product is a potent cause of continued corrosion. Copper exists in two possible states of oxidation, and a copper salt probably acts as an oxygen-carrier or catalyst, and thus promotes the removal of the hydrogen.

General Corrosion and Pitting. It is customary among engineers to distinguish two general types of corrosion. If the whole surface of a metal tube or plate is attacked uniformly, so that the whole tube or plate becomes, in the course of time, slightly thinner, it is customary to speak of the phenomenon as "general corrosion" or "general thinning"; this type of corrosion is usually slow, and causes but little annoyance. Sometimes, however, local and very rapid corrosion occurs at a few points, where the corrosive agency seems to bore into the metal, quickly producing deep pits, and finally causing perforation of the tube or plate; this type is known as "pitting." Possibly between the pits, the surface of the metal may be almost unchanged, so that the total amount of metal attacked in the type of corrosion known as pitting may not exceed that involved in "general thinning"; but it is obvious that pitting will cause the failure of the plate or tube much more quickly.

The cause of pitting varies in different cases. Many occurrences of pitting in steel have been attributable to the presence of mill-scale upon the surface. Steel always comes out of the mill covered with a bluish-black scale, consisting mainly of the oxide Fe_3O_4, caused by the action of steam and air on the hot metal. If the layer of scale is left untouched, the effect of the scale is rather to protect the iron than otherwise. Suppose, however, that the scale is mainly removed, but, through inadvertence, a flake is left on the surface here and there; under such circumstances couples of the type

Iron | Water | Scale

may be set up at these points. Magnetite (Fe_3O_4) is a good conductor of electricity, and is eminently suitable to form the cathode of a corrosion couple. Hence corrosion takes place rapidly at the points where the flakes exist, and rapid pitting occurs.[2] Therefore, if the scale is removed at all, it should be removed completely.

In other cases, the pitting may be occasioned by a grain of some "noble" impurity occurring at the surface of the metal at the point in question. In aluminium bronze, pitting is said to occur around the particles of the compound $CuAl_2$.[1] It is stated that the presence of manganese sulphide or ferrous sulphide in steel occasions pitting for the same reason[2]; certainly iron containing sulphur is very liable to serious corrosion, but it is quite likely that this is due to the sulphuric acid derived from the sulphide particles.[3]

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[1] J. Aston, *Trans. Amer. Electrochem. Soc.* **29** (1916), 449.

[2] G. C. Whipple and M. C. Whipple, 8th *Int. Cong. App. Chem.* **21** (1912), 155; W. H. Walker, *Trans. Amer. Electrochem. Soc.* **14** (1908) 182.

Where the corrosion product has an especially favourable influence upon further corrosion, there is likely to be pitting. For in such cases, if, through any chance circumstance, corrosion commences at one particular spot, it is likely to continue at that spot in preference to others. In brass condenser tubes, it is most important that the basic salts which form the corrosion product should not be allowed to adhere to the tube; normally, they will be carried out of the tubes by the current of water passing through them, but if the water contains foreign bodies such as sand, coke, seaweed, or other débris, these bodies may settle on the surface of a tube, and entrap the basic salts, which will then facilitate further corrosion. If once corrosion is fairly started in a tube, it is very difficult to stop it. Consequently, it is important, as far as possible, to keep foreign bodies out of the tubes.[4]

Atmospheric Corrosion and Tarnish. Hitherto we have considered the corrosion of metals which are in contact, either continuously or periodically, with water. The atmospheric corrosion of objects exposed to the weather in ordinary climates comes under this heading, for here the metal is periodically wetted by rain, and, as oxygen is always present, conditions are most favourable for corrosion.

It is necessary, however, to study also the changes in the surface of metals exposed to the air, but never brought in contact with *liquid* water. The words "liquid water" are used purposely, for the presence of water vapour in the air is, in most cases, essential for any change at all; even a highly reactive metal like potassium remains unchanged when exposed to perfectly dry, pure air.

Most metals, however, undergo some surface oxidation when exposed to ordinary damp air, the change being usually more marked in damp and hot climates. The changes are nearly always accelerated by the presence of acid gases, such as hydrogen chloride, sulphur dioxide and carbon dioxide, which occur in the atmosphere near many manufacturing towns, and sometimes by the presence of ammonia, which occurs in the air near stables. These facts suggest that the changes really take place in a film of adsorbed moisture, which is known to exist upon the metal, according to the electrochemical principles discussed above. Possibly the presence of the acid or alkaline substances mentioned serves to increase the conductivity of the film. Further research upon the mechanism of atmospheric corrosion is, however, needed.

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[1] C. H. Desch, *Trans. Faraday Soc.* **11** (1916), 202.

[2] K. P. Grigorowitch, *Rev. Met.* **12** (1915), 242 (abstract).

[3] G. T. Moody, *Proc. Chem. Soc.* **25** (1909), 34. Whilst Moody's views on the general subject of corrosion are not usually accepted, he is probably right on this particular point.

[4] G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 104.

Usually the effects of exposure to the air are extremely slight. They are most obvious to the eye in the case of metals like copper and lead which have coloured oxides. Both these metals darken and lose their lustre when exposed to air; but the oxidized layer (the composition of which probably does not correspond to any oxide known in the massive state) is really extremely thin. It becomes thicker at high temperatures; copper exposed to heat often shows the colours characteristic of thin oxide films.

Zinc and aluminium, which do not form coloured compounds, alter less in appearance as a result of exposure. Actually, however, they suffer superficial oxidation. Aluminium, as has been mentioned, at once develops a thin oxidized skin, which, however, is so compact and adherent that it prevents further oxidation; consequently aluminium usually keeps its metallic lustre better than many of the metals far above it in the Potential Series.

On the other hand, when the corrosion product is hygroscopic, it may absorb water from the air and corrosion will continue at an increasing rate. This occurs in the case of zinc in the presence of hydrogen chloride, copper in the presence of ammonia, nickel in the presence of sulphur dioxide, and sodium in pure moist air.[1]

The Corrosion of Alloys. It has been mentioned above that the presence in a reactive metal of a noble impurity occurring as a separate phase, is likely to favour corrosion, by allowing the formation of a corrosion couple. On the other hand, the presence of a noble metal in solid solution will—as long as it remains in solid solution—tend to retard the passage of the active metal into the ionic condition.

Some of the alloys consisting of mixed crystals withstand corrosion remarkably well. Monel metal, an alloy of nickel and copper, is far more resistant both to acids and alkalis than either constituent.

Various elements, e.g. chromium, are sometimes added to iron and steel in order to increase the resistance to corrosion. Steel containing copper also withstands the action of weather better than ordinary steel; here it is possible that the copper is not in solid solution, but forms a continuous network between the grains, thus restricting corrosion to the outside layer of grains.[1]

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[1] U. R. Evans, *Faraday Society* (1923).

The effect of corrosion on an alloy containing two metals is naturally rather complicated. Usually the more reactive metal is preferentially attacked, so that the surface layer becomes increasingly rich in the more noble metal. Thus brass, after being "pickled" in acid, is found to have a layer on the surface richer in copper than the interior portions. A rather similar phenomenon, usually styled "dezincification," appears to occur when brass is allowed to corrode in sea-water. A layer rich in copper is found at the surface of the metal, but it is thought by most investigators to be formed indirectly; according to his view both zinc and copper are dissolved at first, and the copper is then redeposited (chemically or electrochemically), a corresponding further quantity of zinc being thus brought into solution. Whatever the mechanism, the corrosion is greatly accelerated at points where the corrosion product containing copper salts is allowed to accumulate on the brass surface. The copper salts appear to function as oxygen carriers. The subject will be further discussed in the section on Brass (Vol. IV).

Very interesting is the action of nitric acid upon gold-silver alloys at 115° C. When $\frac{5}{8}$ of the atoms of the mixed crystals consist of silver, the acid dissolves practically the whole of the silver, the gold being left in a spongy condition. On the other hand, when only half of the atoms consist of silver, the acid is practically without action on the alloy, except at the surface. Apparently, the removal of half the atoms of a space lattice near the surface does not open up the alloy sufficiently for the acid to penetrate into the interior. If, however, $\frac{5}{8}$ of the atoms belong to the soluble variety, penetration can occur, and the attack continues indefinitely.[2]

Does Chemical—as opposed to Electrochemical—Corrosion Exist? From the ascertained facts of experimental electrochemistry, it may be predicted that whenever a non-uniform metallic surface is introduced into a conducting liquid, a current will flow between the cathodic and anodic portions, and will continue to flow until the potential at these portions has become equal. The equalization of potential may occur either

(*a*) through the **accumulation** of adsorbed **hydrogen** upon the **cathodic** portions;

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[1] E. A. Richardson and L. T. Richardson, *Trans. Amer. Electrochem. Soc.* **38** (1920), 221.

[2] See G. Tammann, *Zeitsch. Anorg. Chem.* **107** (1919), 1: **112** (1920), 23; *Zeitsch. Metallkunde,* **13** (1921), 406. Tammann has worked out a most interesting theory of the attack of corrosive agents upon solid solutions, which is not, however, universally accepted.

(*b*) through the formation of a **protective oxide-film,** or other protective film, on the **anodic portions.**

Normally one of these conditions will quickly be arrived at, and there will be no lasting corrosion. If, however, neither (*a*) nor (*b*) occur, the current must continue indefinitely, and this must involve the corrosion of the anodic portions. Of the two factors which would tend to bring corrosion to a standstill:—

(*a*) The *accumulation of hydrogen at the cathodic portions* may be prevented, if

(i) the conditions are such that hydrogen is evolved in gaseous form (e.g. from an acid solution), or if

(ii) dissolved oxygen is able to combine with and continuously remove, the adsorbed (invisible) hydrogen.

(*b*) *The production of a protective film* (total or partial passivity) is unlikely to occur if there are present either

(i) substances which would tend to *dissolve* an oxide-film (e.g. an acid), or

(ii) substances which would tend to *loosen* the film and render it non-protective (e.g. chlorides).

Thus, even if no research had ever been conducted upon the phenomena of ordinary corrosion, our experimental knowledge of the behaviour of single electrodes would lead us to expect corrosion in the majority of conditions under which—in practice—it is met with. The fact that it has been shown possible by Lambert to avoid corrosion by obtaining absolute purity and uniformity in a metal—although of no commercial importance, owing to the rigorous character of the precautions necessary—is certainly an argument in favour of the electrochemical character of corrosion.

Until it has been shown definitely that corrosion occurs under conditions in which the electrochemical theory would fail to predict it, or in a degree which could not be accounted for by that theory, there is little need for the so-called "chemical theories" of corrosion. In the view of the present writer, it is difficult to find a single clearly investigated case which would force us to adopt the hypothesis of chemical corrosion.[1] As soon as such a case has been brought forward—and has been verified by investigators possessed of a complete knowledge of electrochemical theory—he will be prepared to accept the view that chemical corrosion, as well as electrochemical corrosion, can occur; it is quite possible that cases of this kind may be brought up in the near future.

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[1] U. R. Evans, *Engineering,* **114** (1922), 370.

It is perfectly true that certain investigators have already obtained results, which—in the view of these investigators—cannot be interpreted upon the electrochemical theory. In some of these cases, facts have undoubtedly been brought to light requiring further investigation, but it appears probable that this investigation would show them to be capable of explanation on the electrochemical theory. At the same time, it is fair to add that many authorities who have an undoubted experience of corrosion regard the unmodified electrochemical theory as unsatisfactory. Amongst others may be mentioned the members of the Corrosion Committee of the Institute of Metals; the reports of this Committee [1]—which constitute a collection of facts of great value—should be studied by any reader who wishes to regard the subject from both standpoints.

Even if proved to exist, "chemical corrosion" could really be regarded as a special case of "electrochemical corrosion." In the electrochemical corrosion of a divalent metal M by water containing oxygen, the following reactions occur:—

(1) at the anodic portions $M = M^{\cdot\cdot} + 2e$
(2) at the cathodic portions $2H^{\cdot} + 2e = 2H$

followed by

(3) $$2H + O = H_2O$$

The removal of hydrogen leaves the water alkaline, and consequently the metallic hydroxide is precipitated by the change,

(4) $$M^{\cdot\cdot} + 2(OH)' = M(OH)_2$$

Adding up these four equations, we get for the total change,

$$M + 2H^{\cdot} + 2(OH)' + O = M(OH)_2 + H_2O$$

or, writing water in the unionized form (H_2O),

$$M + H_2O + O = M(OH)_2.$$

This is the final result of the change.

If now we imagine corrosion to take place in a chemical manner, that is, without specialized anodic and cathodic areas, we can imagine all the stages of the change

$$M + H_2O + O = M(OH)_2$$

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[1] W. E. Gibbs, R. H. Smith and G. D. Bengough, *J. Inst. Met.* **15** (1916), 37; G. D. Bengough and O. F. Hudson, *J. Inst. Met.* **21** (1919), 37; G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 65; G. D. Bengough and J. M. Stuart, *J. Inst. Met.* **28** (1922).

to occur at the same points of the metallic surface. It can then be expressed conveniently by the single equation just given; but, since the metallic atoms are in an uncharged state before corrosion, and in a charged state after corrosion, the change must still be regarded as in a sense an electrical one—even although the anodic and cathodic areas are identical. One can therefore define the hypothetical "chemical" corrosion as being electrochemical corrosion proceeding under conditions which allow the same areas to function both as cathodes and anodes.

Various special forms of the chemical theory have been devised—mainly to account for the action of certain types of corrosion-product in stimulating corrosion. The accumulation of copper chloride upon brass which is immersed in sea-water undoubtedly accelerates corrosion. It is regarded as acting, in effect, as an oxygen-carrier according to some such series of changes as [1]

$$4CuCl + O = Cu_2O + 2CuCl_2$$
$$CuCl_2 + Cu = 2CuCl$$
$$CuCl_2 + Zn = ZnCl_2 + Cu$$

Similarly, the view has been put forward that colloidal iron hydroxide acts as an oxygen carrier in the corrosion of iron and steel.[2] But in both cases the observed facts can be explained equally well—in the opinion of the present writer—on the electrochemical theory.

Summary. Metals which stand below hydrogen in the Potential Series, are in general attacked by dilute hydrochloric or sulphuric acid, hydrogen gas being liberated; the rate of attack is usually much more vigorous when the metal is impure, or where it is in contact with some more "noble" substance with a low "over-potential" value, a short-circuited cell or "couple" being set up. Metals standing above hydrogen cannot liberate hydrogen as gas, but are in many cases attacked by oxidizing acids, such as nitric or hot concentrated sulphuric.

Some of the more reactive metals are attacked by neutral or alkaline solutions, but usually only in cases where the hydroxide will be soluble in the solutions in question. Several comparatively "noble" metals, like gold and silver, are attacked by potassium cyanide in the presence of air.

Corrosion of common metals by commercial or domestic water-supplies depends normally on the presence of dissolved oxygen; acid waters are usually more corrosive than alkaline, but hard waters usually less corrosive than soft. In the case of many metals, chlorides, which keep the metals active, greatly increase corrosion. Contact with "noble" substances which conduct electricity often sets up corrosion, and strained metals often corrode owing to couples set up near the point of straining. The anodic action of stray electric currents is often very serious.

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[1] G. D. Bengough, R. M. Jones and R. Pirret, *J. Inst. Met.* **23** (1920), 101.

[2] J. A. N. Friend, *Trans. Chem. Soc.* **119** (1920), 932.

Sometimes the water can be treated so as to reduce its corrosive power; addition of alkaline substances or of chromates (which render iron passive), and also the removal of dissolved oxygen, are effective remedies. More often the metal is treated. When iron is covered with tin, lead, nickel, or copper, the coat must be continuous, otherwise the "couple" set up at the point of exposure of the iron will tend to favour corrosion. On the other hand, when a zinc coat is used, it protects the iron even where the latter is exposed, since zinc stands below iron in the Potential Series. The employment of zinc "protectors," and of electrochemical (cathodic) protection depends on similar principles. In the protection by a paint film, a nearly non-conducting, moisture-free film should be aimed at. The nature of the pigment is important; any form of carbon tends to aid corrosion, whilst (in the case of iron) chromates and basic pigments tend to reduce it.

The presence of the "corrosion product" has an important effect on further corrosion. If closely adherent it may shield the metal below; in other cases, it may act (in one of several ways) so as to promote further corrosion. More especially, it may give rise to "pitting," which is far more serious than uniform "general corrosion."

In perfectly dry air, most metals keep bright. In damp air, surface oxidation takes place. At ordinary temperatures the thickness of the oxidized film is small; the dulling is most conspicuous in cases like lead and copper, metals which, in other cases, form coloured compounds. Some reactive metals, like aluminium, become covered with a closely adherent oxide-film, which tends to make them behave like quite "noble" substances.

The question of the corrosion of alloys is complicated. The addition of a "noble" metal as a separate phase tends to promote corrosion by causing a couple, whilst the presence in solid solution reduces corrosion. Thus a trace of copper in water tends to favour the attack of steel, but copper dissolved in the steel materially reduces the corrosion. In the attack of acids upon solid solutions, the relative amount of the two constituents is all important; if the more attackable constituent is in excess, it may be dissolved away preferentially, throughout the volume of the alloy; if present in small amounts, it is dissolved at the surface only, a protective layer rich in the more noble constituent being thus produced.

Electrochemical principles would lead us to expect most of the phenomena of corrosion which are actually observed, and it is probable that nearly all the known cases of corrosion are of the "electrochemical type." Some authorities regard the electrochemical theory as unsatisfactory and believe in direct chemical corrosion; such "chemical corrosion" could, however, be regarded as a special case of "electrochemical corrosion" in which cathodic and anodic areas are identical.

CHAPTER XV

RADIOACTIVITY

In 1896, Becquerel discovered that compounds containing **uranium** emitted rays which were capable of affecting a photographic plate in the same way as light rays, but which readily passed through black paper and other substances opaque to light. About two years later, it was discovered that **thorium** and its compounds possessed similar properties, to which the name "radioactivity" came to be applied. It was also found, by Mme. Curie, that the naturally occurring ores of uranium contained other substances more radioactive than pure uranium itself. After much laborious work, she succeeded in isolating several of these substances, including one especially radioactive substance to which was given the name of **radium**. The discovery of this sensationally active substance awakened great interest in the subject of radioactivity, although, it is right to point out, many of the properties of radium are possessed—in a less marked degree—either by thorium or uranium, elements which have been known for a long time. During the past two decades many other radioactive elements have been proved to exist, so that the number now amounts to at least thirty-nine, whilst new discoveries are reported from time to time.[1] Many radioactive elements, like uranium and radium, are constituents of "uranium ores," whilst others, like thorium and mesothorium, occur in "thorium ores."

The nature of the rays given off by radioactive substances has been carefully studied by physicists. The principal rays can be classified as follows:—

α-Rays. These have been shown to consist of small positively electrified moving particles (α-particles); each particle bears a positive electric charge equivalent to twice the negative charge of an electron, whilst the mass of the particle is about four times that of the hydrogen atom. It is practically certain that an α-particle is identical with the nucleus of the helium atom, that is to say, with the atom of the inert gas helium bereft of two electrons. Gaseous helium has been shown to be formed in radioactive changes in which α-rays are given out, and a quantity of occluded helium is invariably found in uranium ores; apparently, the helium is formed by the union of electrons with α-particles, when the latter are arrested in their course.

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[1] See, for instance, O. Hahn, *Ber.* **54** (1921), 1131; A. Piccard and E. Stahel, *Phys. Zeitsch.* **23** (1922), 1.

β-Rays. These consist of negatively electrified moving particles (β-particles) much smaller than the α-particles. It is practically certain that the β-particles are nothing but free electrons.

γ-Rays. These do not appear to consist of particles at all, but are probably closely connected with X-rays. As already explained in the introduction, X-rays are waves produced when rapidly moving electrons ("cathode ray particles") are brought to a stop by a metallic surface; the disturbance caused by the moving electrons to the electrons of the metallic atoms appears to be the essential cause of production of the X-rays. Now, when an electron (or β-particle) is expelled from the nucleus of a radioactive atom, it probably causes a disturbance of a somewhat similar character. It is not surprising, therefore, to find that γ-rays—very similar in properties to X-rays—are generally produced during the liberation of the β-particles.

δ-Rays are probably merely β-rays moving with very small velocity. They need not be discussed further.

Properties of α-, β- and γ-rays. It has been stated above that the rays were first recognized by their action upon the photographic plate. β-rays have a very powerful action upon the plate, γ-rays a rather less marked effect, whilst α-rays are the least active of the three in this respect. As in the case of the effect caused by light waves, there is no immediate visible change in the appearances of the plate, but when the plate is subsequently treated with a "developer," it darkens where the rays have fallen upon it.

More striking is the effect of the rays in causing certain phosphorescent substances to glow. Certain forms of zinc sulphide become luminous when exposed to α-rays. If a screen coated with zinc sulphide is placed near to a radioactive body, which is giving off α-particles, a visible flash is caused at the point of impact when each separate α-particle strikes the screen; by means of a microscope, it is possible to count the actual number of particles striking a zinc sulphide screen during a given time.[1] β-Rays and γ-rays also render the same substances luminous, but to these rays zinc silicate and barium platinocyanide are more sensitive than zinc sulphide.

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[1] Sir W. Crookes, *Chem. News* 87 (1903), 241; E. Rutherford and H. Geiger, *Proc. Roy. Soc.* 81 [A] (1908), 141.

The α-, β- and γ-rays differ most remarkably in their penetrating matter. The α-rays, consisting of helium nuclei, are easily stopped by matter; the β-particles, being merely electrons, have rather more penetrating power, whilst γ-rays, which are probably "non-material" in character, have still greater power of passing through substances that are usually considered opaque. In all cases it is to be noticed that substances of high atomic weight like lead stop the passage much more effectively than substances of low atomic weight, like aluminium. Gaseous substances—such as air—have naturally far less stopping power than solids, although, in the case of α-rays, the diminution of velocity by even a thin layer of air is very serious.[1]

It must be understood that the α-rays produced by one radioactive element may be expelled with very different velocity from those produced by another, and consequently the α-rays will have different penetrating power in the two cases; the same is true of β-rays and γ-rays emitted by different substances. The following remarks by Soddy are quoted[2] in order to give some rough idea of the relative absorption of the three types of radiation:—

"The α-rays are most easily absorbed. None are able to penetrate a piece of ordinary paper or a few centimetres of air at atmospheric pressure. The β-rays go through thin metal foils with ease, but are for the most part absorbed by a millimetre of lead. The γ-rays are able to pass through a great thickness of metal without complete absorption. The more penetrating types are those of the thorium and radium series, and for these every 1·4 cm. of lead cuts down the radiation to about half its initial value."

If, as is generally believed, the particles penetrating any medium actually pass through the component atoms, one might expect some change to be produced in the medium also. Actually this is found. The most universal effect is a heating of the medium, the kinetic energy of the α-particles being given up, as they stop, to the molecules of the medium in question. The rise of temperature caused by radioactive change is quite appreciable and is largely due to the kinetic energy of the α-particles.[3] Sometimes, however, the α-particles will produce other more striking effects, the atoms composing a molecule being, as it were, knocked away from one another by the projectiles; thus α-rays, passing through water, cause decomposition into oxygen and hydrogen. In other cases, the decomposition may be of a sub-atomic character; it has been found that when α-rays pass through air, or any other gas, the gas becomes a conductor of electricity. This phenomenon is apparently due to free electrons being " knocked away from " the atoms, and the gas thus comes to contain negative ions (free electrons) and positive ions (the residues of the decomposed atoms or molecules). The " ionization " of a gas by α-rays will be further discussed below, because it provides a means of measuring the degree of radioactivity of a substance. It may, however, be mentioned here that both β-rays and γ-rays are capable of producing ionization in a gas, although naturally to a much smaller extent.

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[1] The manner in which the velocity of α-rays diminishes during their flight is described by H. Geiger, *Proc. Roy. Soc.* **83** [A] (1910), 505.

[2] From F. Soddy's "Chemistry of the Radioactive Elements" (Longmans, Green & Co.).

[3] E. Rutherford and H. T. Barnes, *Phil. Mag.* 7 (1904), 202.

The majority of the α-particles appear to be but little deflected in their course by the atoms through which they pass. Probably these comparatively undeflected α-particles do not pass near to the nucleus of any atom. A very small proportion of the whole suffer, however, very marked deflection in their course ; a certain number are thrown off at right angles to their former direction of motion, whilst a few are even more deflected out of their course, deviations of 150° having been observed in the passage of α-rays through gold and silver foil. It is thought that each of these violently deflected particles must have passed very close to the positively charged nucleus of some atom, and thus has come within the zone of electrostatic repulsion. It is, in fact, mainly upon this violent deflection of a small proportion of the particles that our knowledge of the nucleus is based.[1]

We have just seen that bombardment with α-particles may cause :—

(1) Increased molecular movement (heating effect).

(2) Disruption of the molecule (e.g. decomposition of water).

(3) Disruption of the atom (ionization of gases).

There is, however, a further possibility, namely

(4) Disruption of the atomic nucleus.

Rutherford[2] has lately shown that when α-rays are passed through nitrogen, swiftly-moving charged particles (" H-particles ") are emitted, which are probably identical with the nuclei of hydrogen atoms. These particles are thought to be formed by the breakdown of the nitrogen nucleus, and thus the fourth possibility mentioned above has been realized. The discovery marks the apparent solution of a problem which has attracted the attention of mankind from early times, namely the artificial transmutation of one element into another.

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[1] H. Geiger, *Proc. Roy. Soc.* **81** [A] (1908), 174 ; H. Geiger and E. Marston, *Phil. Mag.* **25** (1913), 604 ; E. Rutherford, *Phil. Mag.* **27** (1914), 488.

[2] Sir E. Rutherford, *Proc. Roy. Soc.* **97** (1920), 374 ; Sir E. Rutherford and J. Chadwick, *Phil. Mag.* **42** (1921), 809.

It is important to note that such an "artificial transformation" of one normally stable element (nitrogen) into another has only recently been achieved, and only takes place apparently under exceptionally drastic treatment, namely the bombardment by α-particles moving at the rate of 12,000 miles per second. It must not be confused with the "spontaneous transformations" met with in the radioactive elements themselves, which will shortly be described; these latter transformations—which have been known for two decades—take place continuously and spontaneously, and are unaffected by the conditions under which the radioactive elements exist; in fact, it does not seem to be within the power of man either to accelerate or to stop the spontaneous processes.

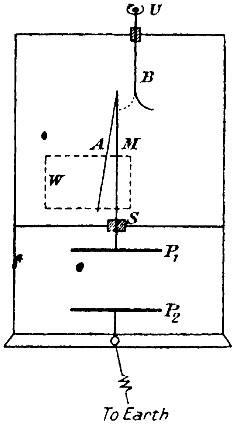

FIG. 90.—Apparatus for Measurement of Radioactivity.

The Measurement of Radioactivity. In order to obtain a measure of the intensity of the radioactivity of a substance, the power of ionizing air possessed by the different rays is generally employed. A simple form of the apparatus used is shown in Fig. 90. It consists of two chambers constructed of metal, the upper one being known as the electroscope, and the lower one being known as the "ionization chamber."

In the electroscope, an upright strip of stiff metal M is supported by a plug of sulphur, S, the sulphur serving to insulate the strip from the casing of the apparatus; at the upper end of the strip, a piece of very thin "aluminium leaf," A, is attached, the lower end of the leaf being free to fly outwards from the strip. The ionization chamber contains two horizontal plates of metal; the upper one, P_1, is connected, through the sulphur plug, to the metal strip M of the electroscope, whilst the lower one, P_2, is connected to "earth."

The bent rod B, also insulated from the metallic casing, can be turned at will so as to touch the strip M. If, when B is in contact with the strip M, a rod of shellac, which has been electrified by rubbing on flannel, is brought into contact with the upper end U, both the strip and the aluminium leaf become electrified also. Owing to the mutual repulsion between like charges, the leaf flies outwards from the strip to a considerable angle; its exact position can be observed through a window (W) in the metal casing by means of a microscope provided with a micrometer scale. The rod B is then twisted again so that it no longer touches the strip.

When once "charged" in this way, the electroscope keeps its charge very well (so long as the ionization chamber contains n radioactive substance) and the leaf continues to point outwards at almost the same angle for many hours. There is, however, a small leakage of the charge to earth, either along the surface of th sulphur plug, or through the air, and consequently the leaf tends t drop slowly towards the strip M, the rate of movement being measured by means of the microscope.

If, on the other hand, a radioactive substance be placed on a little tray on the lower plate P_2, the air in the ionization chambe will become "ionized," and the rate of leakage of electricity from the upper plate to the lower plate (and thus to "earth") increase very much, as is shown by the increased velocity at which th aluminium leaf falls. The rate of fall of the leaf, observed throug the microscope, serves as a measure of the activity of the substanc placed in the tray. The instrument must first be "standardized' by noting the rate of fall when some "standard" radioactive substance, such as pure oxide of uranium, is placed in the ionizatio chamber; it can afterwards be used to examine the activity o unknown materials.

For accurate work, various refinements may be introduced int the apparatus, but the simple form just described gives result sufficiently good for many purposes.

Changes Occurring in the Radioactive Substance. Fro the point of view of the chemist, the actual rays given out b radioactive substances are of much less interest than the remarkabl changes which occur in the substances themselves—changes whic are evidently closely connected with the loss of the α- and β particles.

When a solution of freshly purified uranium nitrate is allowed t stand for a few days, it slowly gives off α-rays, and there appears i the liquid small quantities of another metal, uranium X_1, whic was not there before. Uranium X_1 differs from the original uraniu ("uranium I," as it is called) in chemical, as well as radioactiv properties. For instance, if a little ferric salt is added to a solutio containing uranium I and uranium X_1, followed by excess o ammonium carbonate, the whole of the uranium X_1 is precipitated along with the iron, whilst the uranium I remains in solution. B filtration, therefore, it is possible once more to free the solutio from the impurity (uranium X_1) and start again with pure uraniu I nitrate. After a few days, however, it is found that a fres amount of uranium X_1 has appeared in the solution, nor is an means known whereby this transformation of uranium I into uranium X_1 can be prevented.

Uranium X_1, unlike uranium itself, yields no α-rays, but gives off feebly penetrating β-rays; in doing so, it gives rise to another substance uranium X_2, having chemical properties different from those of either uranium I or uranium X_1. Uranium X_2 has very considerable β-ray activity, and each atom, as it loses a β-particle, becomes converted to a fourth substance, uranium II, indistinguishable in chemical properties from the original uranium I, but differing in radioactive character. Uranium II is believed, in its turn, to become transformed to a substance known as ionium, which appears, in due course, to give birth to radium. It is practically certain that the radium which is always found in uranium ores has been formed from uranium—in the course of ages—in this way. The growth of radium from uranium has now been demonstrated in the laboratory.[1]

The Unchangeable Velocity of Radioactive Change. Before tracing this curious "genealogical table" any further, it is well to inquire whether the transformations, which have just been described, could not be accounted for in a purely chemical manner. For, although uranium X_1 may differ from uranium I, it does not differ in nearly so striking a fashion as sodium chloride differs from sodium metal and chlorine gas. The change of uranium into uranium X_1 does, however, seem to be essentially different from that of "Sodium + Chlorine" into sodium chloride. For the change proceeds in the first case in one direction only. Uranium X_1 can never be turned back into uranium I, whereas sodium chloride can be decomposed once more into sodium and chlorine. In another way "radioactive transformations" differ very much from ordinary chemical changes. Radioactive processes go on at a velocity which is entirely independent of temperature, of the presence or absence of solvents or catalysts, and even of the state of combination in which radioactive element exists; a given quantity of uranium gives rise to the same amount of uranium X_1 each day, whether the uranium exists as nitrate, as chloride, or as pure metal. On the other hand, the velocity of ordinary chemical processes is, as a rule, greatly affected by changes of temperature, whilst the presence of a solvent is often a determining factor in the change. One seems justified, therefore, in thinking that radioactive changes are essentially different from chemical changes, and the only explanation which appears to fit all the facts is that radioactive changes are "sub-atomic" in character.

The rate at which one radioactive substance (the "parent") gives birth to another has been shown to be closely connected with the rate at which the parent substance sends forth α-particles or β-particles. There seems to be no doubt that it is only those atoms of the parent which have lost an α-particle or β-particle that become transformed to the new substance, the other atoms of the parent remaining unchanged. The proportion of the atoms of the "parent" substance, which become transformed each minute, varies, however, remarkably in different cases. It is customary to express the rate of radioactive change of a substance by stating the time required for half the substance present to undergo transformation. This is called the "**period of half-change.**" The period of half-change of uranium I is 6×10^9 years; it would be necessary to wait 6×10^9 years before a uranium I preparation could become half transformed to uranium X_1. Thorium has an even longer period of half-change, about $1{\cdot}7 \times 10^{10}$ years. On the other hand, uranium X_1 has a period of 24·6 days, whilst the period of uranium X_2 is 1·1 minutes. Nor is this by any means the shortest period known. A substance called thorium C' suffers half-change in about 10^{-11} seconds; clearly such a substance cannot be isolated, our belief in its existence being founded on indirect evidence.

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[1] F. Soddy and A. F. R. Hitchins, *Phil. Mag.* 30 (1915), 209.

During the period of half-change, exactly one-half of the atoms which existed in a preparation at the start suffer change. Thus, if we start with a fresh preparation of uranium X_1, at the expiration of 24·6 days one-half of the atoms of uranium X_1 have suffered change to uranium X_2, and one-half survive. At the end of a further 24·6 days, one-half of these surviving atoms have suffered change and only one-quarter of the original atoms remain. At the end of a third period of 24·6 days, we have only one-eighth of the original number surviving. We can write this result in tabular form thus:—

After 24·6 days, $\frac{1}{2}$ of the atoms survive.
After $2 \times 24{\cdot}6$ days, $\frac{1}{4}$ of the atoms survive.
After $3 \times 24{\cdot}6$ days, $\frac{1}{8}$ of the atoms survive.
After $4 \times 24{\cdot}6$ days, $\frac{1}{16}$ of the atoms survive.
After $n \times 24{\cdot}6$ days, $\frac{1}{2^n}$ of the atoms survive.

The amount of uranium X_1, therefore, gradually diminishes until it becomes inappreciably small, unless, of course, there be uranium I present, from which fresh uranium X_1 can be formed.

Some physicists prefer to express the radioactivity of an element by means of the "average life of an atom." The average life of an atom—that is, the average of the periods during which all the atoms of a substance survive before suffering transformation into some other substance—is always 1·443 times the "period of half-change." Thus the "average life" of the uranium X_1 atom is

$$24·6 \times 1·443 = 35·5 \text{ days.}$$

The period of half-change gives a very good idea of the relative radioactivity of the different radioactive elements. Those with long periods clearly change only slowly, and thus send out comparatively few α-rays or β-rays, as the case may be, whilst a similar quantity of a short-period element sends out rays much more profusely. Moreover, the α-rays sent out by the slowly-changing elements have a much lower velocity, and consequently much smaller penetrating power, than those provided by the elements which change rapidly. In fact it is possible to calculate the period of half-change from the velocity of the α-rays expelled from the substance—a method very useful in cases, like that of the thorium C′ referred to above, where the period cannot be determined directly.

Since, therefore, the short-period elements are much more active than the elements with long periods, it is easy to understand why radium, which has a period of half-change of only 1,690 years, should be much more active than uranium, which has a period of 6×10^9 years. Of course those members of the series which have half-change periods measurable in days or hours, would—if they could be prepared in the same quantities as radium—constitute an even more potent source of radioactivity. But preparations containing such bodies necessarily have only temporary activity, and soon become transformed to other substances. Moreover, there is no means of obtaining short-lived bodies except in very minute quantities, since, owing to their very instability, the short-lived bodies exist in the ores of uranium and thorium in much smaller quantities than the long-period elements.

Radioactive Series. It is now possible to resume the study of the "genealogical table" of the elements derived from uranium I as "ancestor." The most probable version of the facts is given below in tabular form.[1] The table also shows the somewhat analogous series of elements which spring from thorium as original ancestor. Subsequent work may show that the two lines are really separate branches, as it were, of the same family; but the facts, so far as they are known at present, do not indicate this as being likely.

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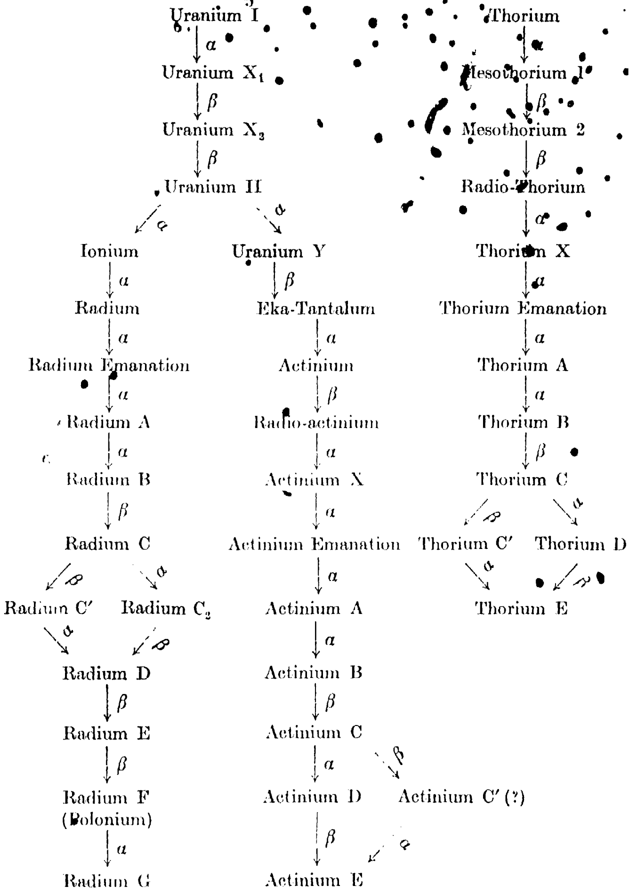
[1] J. H. L. Johnstone and B. B. Boltwood, *Phil. Mag.* **40** (1920), 50, consider that the series as here given does not account for all the facts. They consider various possible modifications of the table, with special reference to the point where the "branching" of the series into the radium and actinium branches occurs; but they conclude that "none of the theories appear to satisfy the necessary requirements." Conceivably the actinium family forms a series distinct from the uranium family. See G. Kirsch, *Phys. Zeitsch.* **21** (1920), 452; A. Piccard and E. Stahel, *Phys. Zeitsch.* **23** (1922), 1.



The letters α or β placed beside each of the arrows indicate whether an α- or β-particle is expelled at the moment of the transformation in question. It will be noticed that uranium II gives rise to two separate products, and the series branches at this point. There is, however, a little doubt as to the exact state of affairs here. Lower down, another parent, radium C, also gives two products, one through the expulsion of an α-particle, and the other through the expulsion of a β-particle; but here it is probable that each product gives rise to radium D at the next step. A similar "branching" occurs in the thorium series, where thorium C gives rise to two separate elements.

Three of the elements included in the table just given are gaseous at ordinary temperatures, namely radium emanation, actinium emanation and thorium emanation. All these are chemically inert gases, similar in chemical properties to the inert gases of Group O of the Periodic Table, but very active in producing rays. The most important of the three is radium emanation, which is produced directly from radium.

When a salt of radium is dissolved in water, and a current of air is passed through the solution into the ionization chamber of a charged electroscope, it is found that the air has become a good conductor of electricity, for the leaf of the electroscope drops very rapidly. This is explained by the fact that the air has carried out with it some of the emanation or radioactive gas, which is being produced continually by the radium of the solution.

Although chemically inert, radium emanation is unstable in the radioactive sense, and the atoms gradually change to atoms of the solid radium A, which in turn gives rise to radium B; and in due course radium C also appears. These substances cling to the walls of the vessel containing the emanation, or settle to the bottom, forming an "active deposit." The production of an active deposit on a substance immersed in radium emanation occurs most readily if the substance in question is negatively electrified. If, in the experiment just described, all the gaseous emanation is afterwards swept out of the "ionization chamber" by a current of ordinary air, the electroscope continues to indicate the presence of radioactive substances, which are, in fact, the radium A, radium B and radium C clinging to the plates and walls of the chamber. All these substances are highly active, but—just because they are highly active—they are short-lived, and finally change to the comparatively long-lived and very feebly active substance, radium D. However, even this substance undergoes a slow transformation, radium E being produced; radium E changes into polonium (or radium F), which in turn produces radium G, the "end-product" of the series; radium G is indistinguishable in chemical properties from pure lead, and it is probable—as will be shown below—that much of the so-called "lead" which is always found in uranium ores, is really radium G.

It should be pointed out that the quantity of active deposit is usually so small as to be absolutely invisible; its presence upon the surface of a substance, or on the walls of a vessel, is only detected by the ionization and other effects produced by the rays given off.

Radioactive Equilibrium. If a mass of uranium I is imagined to be taken and shut up for a few million years in a place from which none of the members of the series (not even the volatile radium emanation) can escape, it is clear that in the course of time, all the members of the series down to radium G, the end-product, will make their appearance. At first, the later members of the series will be present only in small amounts, but gradually the quantities of these later members will increase, until a state of "radioactive equilibrium" is arrived at. In a state of "radioactive equilibrium," the amount of every member in the series, except the first and last, remains approximately constant, the number of atoms of any given substance lost, during any given time, through change into its "offspring" being roughly equal to the number of fresh atoms derived by the transformation of the "parent." For instance, the number of atoms of ionium turning to radium each day would be equal to the number of atoms of radium changing to radium emanation in the same time; the amount of radium present would therefore remain constant. It follows that when a state of radioactive equilibrium is reached, the ratio of radium to uranium 1 ceases to increase further, but remains roughly constant, being independent of any further period during which the substances are stored.

Most of the uranium ores found in the rocks of the earth have been "stored" under suitable conditions, and for a sufficient time, to bring about approximate "radioactive equilibrium." In these cases, the ratio of the radium to the uranium should have become practically constant. Careful analysis[1] has shown that, in the majority of uranium ores occurring in rocks of different ages and different localities, the ratio

$$\frac{\text{Radium Content}}{\text{Uranium Content}}$$

varies between $3{\cdot}341 \times 10^{-7}$ and $3{\cdot}320 \times 10^{-7}$. The practical constancy of the value in such cases certainly supports the view that the whole of the radium in the minerals has been derived by the breakdown of the uranium atoms. The ratio of actinium to uranium in minerals is also found to be constant.[2]

On the other hand, the amount of "lead" (or, properly, of radium G) found in the minerals increases with their age. In minerals found in rocks which solidified in "Carboniferous" time, the ratio

$$\frac{\text{“Lead” Content}}{\text{Uranium Content}}$$

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[1] B. Heimann and W. Marckwald, *Phys. Zeitsch.* **14** (1913), 303. Recent researches by S. C. Lind and L. D. Roberts, *J. Amer. Chem. Soc.* **42** (1920), 1170, put the ratio of radium and uranium in radioactive equilibrium at $3{\cdot}40 \times 10^{-7}$.

[2] S. Meyer and V. F. Hess, *Sitzungsber. Akad. Wiss. Wien.* **128** [2a] (1919), 909.

is 0·041; those which were formed in the preceding "Devonian" epoch have a higher ratio, 0·045; "Silurian" minerals carry lead in the ratio 0·053, whilst the oldest rocks of all, dating from "Pre-Cambrian" times, contain lead and uranium in ratios varying from 0·12 to 0·20. This increase of "lead" with age is thought to indicate that the lead-like constituent of the ores (radium G) is really the end-product, and does not tend itself to decay giving rise to other substances.[1] There is, of course, no means of proving definitely that radium G does not undergo a very slow change; but as far as we can tell, it is stable.

It is worth noticing at this point that the property of radioactivity is mainly confined to elements of high atomic weight, and as we pass to atoms of atomic weight less than 206, the atoms appear for the most part to be stable. It is true that salts of potassium and rubidium do give off β-particles, but there is no definite evidence that they come from the atomic nucleus, or that they indicate a change analogous to those occurring in radioactive substances. There are also facts known which suggest that copper may have a species of radioactivity,[2] but this question must be regarded as still undecided.

In all uranium ores, the long-lived members of the series, such as uranium I, ionium and radium, are present in far greater amount than those members which have atoms of short average life. A little consideration will show that this must necessarily be the case. A consequence is that, whilst the long-lived members of the series can best be isolated by extraction from the naturally occurring ores, the short-lived members are practically never prepared in this way; they can, however, be obtained in small, often invisible, quantities by the method of "growth" in the laboratory—that is to say, by storing a preparation containing a suitable long-lived "ancestor"—until a perceptible quantity of the short-lived body has been formed, after which it is separated by appropriate chemical or physical means. For instance, radium A, B and C would—in practice—be prepared in the laboratory from a salt of radium by allowing the emanation to produce an active deposit upon a wire or on the side of the vessel; they would not be extracted directly from a naturally occurring uranium ore. Similarly in the case of the thorium series, the only elements sufficiently permanent to be worth extracting direct from thorium ores are thorium itself and mesothorium I. The more short-lived members, if required, must be grown in the laboratory. The table at the end of the chapter, which indicates the method of preparing each radioactive element, makes this point clear.

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[1] A. Holmes, *Proc. Roy. Soc.* **85** [A] (1911), 248; B. B. Boltwood, *Amer. J. Sci.* **23** (1907), 77. The ratio of thorium to lead is discussed by A. Holmes and R. W. Lawson, *Phil. Mag.* **28** (1914), 823.

[2] G. Hoffmann, *Ann. Phys.* **62** (1920), 738.

Since the short-lived bodies are usually produced in quantities so small as to be unweighable and invisible, there is naturally some difficulty in separating them chemically from the much larger amounts of long-lived elements with which they are usually mixed. Where a mere trace of some radioactive substance has to be precipitated from a solution, it is usually best to add a small quantity of some non-radioactive metal which would also be precipitated under the same conditions. For instance, if we desire to separate a trace of uranium X_1 from uranium I by precipitating the former with ammonium carbonate, it is best—as mentioned above—to add a little iron (ferric) salt to the solution, and then to add the ammonium carbonate. The precipitate (consisting mainly of ferric hydroxide) affords the necessary nuclei for the precipitation of the metal uranium X_1, and the preparation of that metal, although greatly diluted with inactive iron, is at least tolerably free from uranium I and other radioactive impurities.

Closely connected with the method just described is the process of separating by selective adsorption. If a solution containing actinium B, actinium C, and actinium D, is shaken with animal charcoal, the actinium D is taken up by the charcoal, whilst the other substances remain in solution. A rather similar method has been applied to separate traces of uranium X_2 from uranium X_1; the solution is filtered through moist tantalic acid; tantalum is chemically related to uranium X_2, and the tantalic acid adsorbs the uranium X_2 whilst the uranium X_1 passes through.

Radioactive Elements and the Periodic Table.[1] It was explained in the introduction that the Atomic Number of an element (the number which decides the place in which the element is to fall in the Periodic Table) is equal to the number of electrons surrounding the nucleus; consequently, if the atom as a whole is to be electrically neutral, the Atomic Number must also be equal to the "net positive charge" of the nucleus. If this be accepted, it becomes possible to predict the chemical character of the product of each stage of radioactive change.

Uranium I is an element belonging to Group VIA of the Periodic Table, and has a positive valency of 6. Its Atomic Number is 92. The element, as stated above, gives off α-rays, a new metal uranium X_1 being left behind. If one α-particle is given off from each atom which undergoes change, and each α-particle has a positive charge equivalent to twice the charge of the electron, then the net positive charge of the nucleus is reduced by two units. In other words, the atomic number is reduced from 92 to 90. But a reference to the Periodic Table given in the Introduction (page 24), will show that the square corresponding to the Atomic Number of 90 is already occupied by the element thorium. Therefore, we should expect uranium X_1 closely to resemble thorium in chemical properties. Experimental investigation has shown that it is not merely similar, but chemically identical. Uranium X_1 differs from thorium only in radioactive properties, and in atomic weight; the atomic weight of uranium X_1 must clearly be 4 units less than uranium (238), since the mass of the α-particle (or helium nucleus) is 4; therefore the atomic weight of uranium X_1 is 234, whilst that of thorium is 232. It is thought, therefore, that the uranium X_1 atom differs from the thorium atom in the mass and size of the nucleus, but that the "net charge" of the nucleus is the same in each case; this means that the number of electrons outside the nucleus is the same in each case, and, if the arrangement of the electrons is similar, it is easy to understand why both elements have identical chemical properties. Uranium X_1 is said to be an "**Isotope**" of Thorium.

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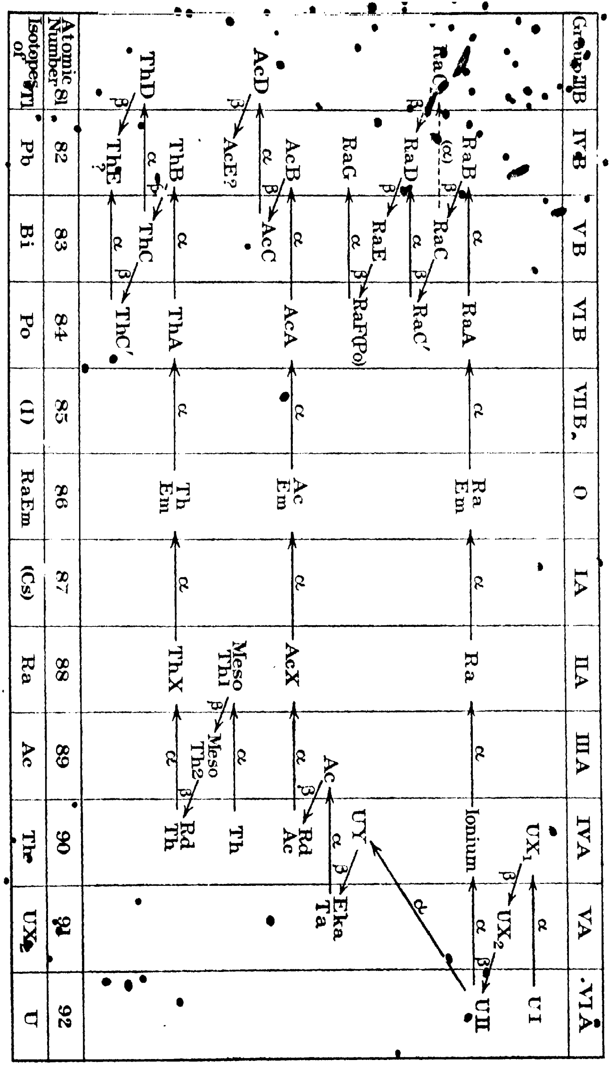
[1] F. Soddy, *Trans. Chem. Soc.* **115** (1919), 1.

The chemistry of uranium X_1 can therefore be summed up in a single sentence: "it is a tetravalent element of Group IVA, chemically identical with thorium." The same line of reasoning can now be applied to predict the properties of the next radioactive element. Uranium X_1 emits a β-particle, producing uranium X_2. The loss of a negatively charged β-particle must result in the increase of the net positive charge of the nucleus by one unit, and therefore in the increase of the atomic number by one to 91. Hence we may expect to find uranium X_2 in the space marked 91 in the Periodic Table; that means that it will be a pentavalent element belonging to Group VA. This fact also has been verified. Uranium X_2 is a metal generally similar to tantalum, which stands above it in the same group, although not, of course, chemically identical (or isotopic) with it.

Uranium X_2 loses another β-particle and gives rise to uranium II. According to the same principles, uranium II should have an atomic number of 92 and thus share a space in the Table with uranium I. This is found to be the case. Uranium II is actually chemically identical with uranium I, although its atomic weight is lower than that of uranium I by about four units, the weight of one α-particle (for the loss of weight due to the expulsion of the two β-particles can be neglected). In short, uranium II is an isotope of uranium I.

The properties of the products of further change can be predicted according to the same rule; *the loss of an a-particle always causes a shift of two places to the left* in the Periodic Table, whilst *that of a*


Group
IIIB
IVB
VB
VIB
VIIB
0
IA
IIA
IIIA
IVA
VA
VIA
U I
UX₁
UX₂
U II
Ionium
Ra
Ra Em
RaA
RaB
RaC
RaC'
RaC₂
RaD
RaE
RaF(Po)
RaG
UY
Eka Ta
Ac
Rd Ac
AcX
Ac Em
AcA
AcB
AcC
AcD
AcE?
Th
Meso Th1
Meso Th2
Rd Th
ThX
Th Em
ThA
ThB
ThC
ThC'
ThD
ThE?
α
β
(α)
Atomic Number
81
82
83
84
85
86
87
88
89
90
91
92
Isotopes of
Tl
Pb
Bi
Po
(I)
RaEm
(Cs)
Ra
Ac
Th
UX₂
U

β-particle causes a shift of one place to the right. The discovery of the rule, which was made independently by Soddy and Russell in England, and by Fajans in Germany, has been of the very greatest importance in correlating the chemical and radioactive properties of the elements.

The effect of these changes is shown in tabular form on page 443. It will be noticed that the application of the rule brings radium into Group IIA; radium is, in point of fact, a divalent metal, chemically similar, although not identical with, barium. It likewise brings radium emanation (also called niton) into Group O, along with the inert gases helium, neon, argon, krypton and xenon—a position which entirely accords with the chemical properties of the emanation.

The rule can furthermore be applied to the actinium branch of the uranium series, and also to the thorium series, and never fails to indicate results in accordance with experimentally determined facts.

In the table just given, all the radioactive substances in any given vertical column, are isotopic with one another, having the same atomic number and therefore sharing the same square in the Periodic Table proper. In certain cases this square is also occupied by some common element, such as thallium, lead or bismuth, which displays no radioactive properties and which is also found in nature in large quantities far apart from the radioactive elements.

It will be noticed that there appear to be seven radioactive elements isotopic with lead, whilst there are five isotopic with polonium, and five isotopic with thorium. In each case, the isotopes appear to possess identical chemical properties, but differ, usually, in atomic weight, as well as in radioactive behaviour. Since the chemical properties of isotopes are identical, it appears impossible—at any rate, at first sight—to separate, by chemical means, two isotopic substances occurring together in a mixture. For they will both be precipitated by the same reagents, and redissolved under identical conditions. Nevertheless it is possible, in many cases, to obtain individual isotopes in a pure state, by indirect means. For instance, radiothorium occurs along with thorium, in thorium ores, and no amount of industry will enable us to separate the radiothorium from the thorium by chemical methods. But mesothorium I also occurs in the ores, and can be separated fairly easily from the thorium; if the mesothorium salt solution is then stored for a few months, radiothorium is developed spontaneously in it, and can be separated from the mesothorium without serious trouble. In this way, radiothorium, free from thorium, is obtained.

It will be understood, from a glance at the table just given, why the end-product of the radium family (radium G) must be an isotope of lead; for the preceding member (polonium), which undoubtedly belongs to Group VIB, certainly gives off α-rays which would throw radium G into Group IVB. Radium G should differ in atomic weight from uranium I by 8 × 4 = 32 units, since eight α-particles are given off in the production of radium G from uranium I. The atomic weight of the end-product, therefore, should be 238 − 32 = 206. The atomic weight of ordinary lead derived from commercial lead ores is 207·2. If, as has been assumed above, the lead-like element occurring in uranium ores is really radium G, its atomic weight should be lower than that of ordinary lead. The atomic weight of the so-called "lead" derived from uranium ores existing in different parts of the world has been determined, and has been found to vary between 206·4 and 206·8.[1] It is probable, therefore, that the "apparent lead" of uranium ores does consist largely of the isotope, radium G, which has been derived from the uranium by a process of radioactive decay.

Now lead occurs also in thorium ores. If the thorium ores contain more thorium than uranium, the atomic weight, instead of being abnormally low, is usually abnormally high, in one case reaching 207·9.[2] This "lead" probably consists in part of the end-product of the thorium series, Thorium E, an isotope of lead, which, being derived from thorium (atomic weight 232) by the loss of six α-particles, should have an atomic weight

$$232 - (6 \times 4) = 208.$$

It has been suggested that ordinary lead, with atomic weight 207·2, may be a mixture of "uranium lead" (of atomic weight about 206) and "thorium lead" (of atomic weight about 208). The fact that ordinary lead behaves as a single substance in all chemical reactions constitutes no valid objection to this view, because the two isotopes would be chemically inseparable, and would remain mixed in the same proportions—no matter in what chemical changes the lead is made to take part.

Isotopes of the Non-radioactive Elements. The suggestion just made is really a special case of a more general theory that has now the support of many eminent chemists and physicists. As early as 1815, Prout pointed out that a large proportion of the atomic weights lay close to whole numbers. Since that time, more accurate determinations of atomic weights have tended to confirm the statement of Prout. If we take as the standard O = 16·000, we have

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[1] T. W. Richards and M. E. Lembert, *J. Amer. Chem. Soc.* **36** (1914), 1329; T. W. Richards and C. Wadsworth, *J. Amer. Chem. Soc.* **38** (1916), 2613.

[2] K. Fajans, *Zeitsch. Elektrochem.* **24** (1918), 163. See also F. Soddy and H. Hyman, *Trans. Chem. Soc.* **105** (1914), 1402.

H = 1·008
He = 4·00
C = 12·005
N = 14·008
F = 19·0
Na = 23·00
P = 31·04
S = 32·06
Ca = 40·07

Now this approximation to whole numbers can hardly be accidental. Nevertheless, there are some very notable exceptions; for example, the atomic weight of chlorine has been determined with great accuracy and is found to be 35·46. Among the heavier elements, the exceptions become exceedingly common.

If, however, it is possible to believe that "chlorine," for instance, is a mixture of two isotopes inseparable by any chemical method, it is quite possible that each of the isotopes have an atomic weight which is a whole number, and that the value 35·46 only represents the average weight of the atoms composing the mixture. The same possibility would apply to other apparent exceptions to Prout's generalization.

In order to settle this question, it is necessary to consider whether isotopes—in spite of their apparent identity of chemical character—could not be separated in some way. There are theoretical reasons for thinking that even the purely chemical properties of isotopes may differ to a minute extent; but the differences have hitherto proved to be too slight to be capable of detection, and even if discovered would almost certainly be quite insufficient as a basis of a separation process.[1] The same applies to the electrochemical properties; it has been found, for instance, that the potential of an electrode coated with radium G peroxide is not appreciably different from one covered with lead peroxide.[2]

Attempts have been made to carry out the fractional crystallization of lead nitrate containing radium G nitrate, but no separation has been effected; for the molecular solubilities of the two salts are identical, and therefore the crystals deposited contain atoms of the two isotopes in exactly the same proportions as they exist in the solution.[3]

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[1] F. A. Lindemann and F. W. Aston, *Phil. Mag.* **37** (1919), 523.

[2] G. von Hevesy and F. Paneth, *Monatsh.* **36** (1915), 795.

[3] T. W. Richards and N. F. Hall, *J. Amer. Chem. Soc.* **39** (1917), 531; T. W. Richards and W. C. Schumb, *J. Amer. Chem. Soc.* **40** (1918), 1403; K. Kajans and M. Lembert, *Zeitsch. Anorg. Chem.* **95** (1916), 297.

The mass of the atoms of two isotopes differs, in most cases, by an appreciable amount. It is of interest to notice that the specific gravities of the isotopes, lead and radium G, also differ, standing to one another in the ratio of the atomic weights, so that the atomic volume of the two isotopes is identical.[1] It is upon the difference in atomic mass that the most hopeful scheme for the separation of the isotopes depends. No success has yet been met with in the separation of radioactive isotopes, but efforts made to separate the lighter elements, such as chlorine, into two components have been so far successful as to indicate—in a fairly satisfactory manner—that several of the so-called "elements" really consist of atoms of at least two different kinds.

If a gas consists of a mixture of two isotopes, the more mobile constituent should be capable of diffusing through a porous partition slightly more readily than the heavier constituent. By a process of "fractional diffusion," therefore, repeated many times, we might hope to resolve the mixture into the two constituents. The process is, however, a most laborious one, because the difference in diffusive powers is extremely small. Nevertheless, in 1913–14, Aston obtained results which led him to believe that the inert gas, neon, could be separated, in this way, into two isotopes; unfortunately the war prevented the work of separation from being completed. More recently, Harkins[2] has applied a similar method to the resolution of chlorine. By the continued fractional diffusion of hydrogen chloride, he separated the gas into a light and heavy portion, which are regarded as containing two varieties of chlorine atoms, of atomic weight 35 and 37 respectively. A rather similar method has lately been applied to separate mercury into a light and heavy portion; although the *vapour pressure* of the isotopes is identical, the *velocity of evaporation* is greatest in the case of the lighter isotope. By repeated fractional evaporation of ordinary pure mercury a separation into two portions, differing in density by as much as 0·49 per cent. has been obtained.[3]

Much more definite results, however, are obtained by Aston, through the employment of an electrical method based upon an apparatus known as the "**mass spectrograph.**"[4] It was explained in the introduction that when an electric discharge passes between metal electrodes through a gas at very low pressure, free electrons ("cathode rays") are shot out from the cathode;

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[1] T. W. Richards and C. Wadsworth, *J. Amer. Chem. Soc.* **38** (1916), 221.

[2] W. D. Harkins, *Nature*, **105** (1920), 230.

[3] J. N. Bronsted and G. Hevesy, *Phil. Mag.* **43** (1922), 31.

[4] F. W. Aston, *Phil. Mag.* **38** (1919), 707; **39** (1920), 611; **40** (1920), 628; **42** (1921), 140, 436; *Sci. Progr.* **15** (1920), 212; *Trans. Chem. Soc.* **119** (1921), 677; F. W. Aston and R. H. Fowler, *Phil. Mag.* **43** (1922), 514.

it has been found that under the same circumstances positively charged particles ("positive rays") are also produced—probably through collision of the cathode ray particles with the gaseous molecules. The positive ray particles travel in the opposite direction to the cathode rays, namely *towards* the cathode; if the cathode is pierced by an aperture, a pencil of the particles can be obtained and their properties examined. Most of the positive ray particles appear to be atoms or molecules which have lost one or more electrons.

A stream of positive ray particles can be deflected in their course by an electrostatic field, and also by a powerful magnetic field, although they are far less sensitive to such influences than the lighter cathode ray particles, and, being positively charged, are drawn out of their course in the opposite direction. The "**mass spectrograph,**" shown diagrammatically in Fig. 91, is an apparatus in which a thin ribbon-like beam of positive ray particles admitted through the slits S_1 and S_2 suffers deflection, first by an electrostatic field (provided by the electrified plates P_1, P_2) and then by a magnetic field provided by the magnet M, being finally brought to focus upon the surface of the photographic plate, AB. The arrangement is such that the position on the plate of the point where the rays strike the sensitive surface depends upon the ratio

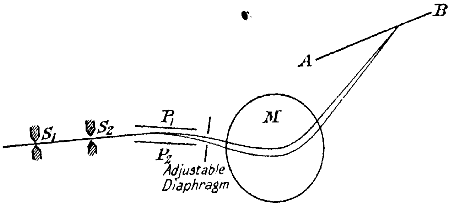

FIG. 91.—Mass Spectrograph (Diagrammatic).

$$\frac{\text{charge upon a particle}}{\text{mass of a particle}}$$

If we confine our attention for the moment to particles which carry unit charge (having lost one electron only), then the heavier particles will strike the plate at the near end (A), the particles of intermediate mass in the middle, and the light particles towards the far end (B). It is obvious that if the stream consists of particles of one size only they will all strike the plate at the same point, and we shall, on developing the plate, get a "positive ray spectrum" consisting of a single line. If a few of the particles carry a double charge a second fainter line may be produced at some distance from the first, and possibly a third line, still fainter and more remote, may be produced, if particles with three charges are present. But, so long as all the particles are of one size, the spectrum produced is simple. If, however, the particles consist of two kinds differing from each other slightly in mass, the result is far more complicated. Each of the lines will become double. By studying carefully the positions of the lines it is possible to arrive at the masses of the particles that cause them. The "positive ray spectrum" of chlorine, for instance, has been interpreted as showing that chlorine consists of two kinds of atoms, having atomic weights 35 and 37 respectively; there are no particles of atomic weight 35·46 present, although the two kinds of particles must be mixed in such a proportion that the *average* weight of the atom is 35·46. On the other hand, it has been shown, by means of the positive-ray spectrum, that hydrogen, helium, carbon, nitrogen, oxygen, phosphorus and sulphur are all "pure" elements, consisting of atoms of one size only. All these are cases, it should be noticed, in which the atomic weights have long been known to lie very close to whole numbers. Elements like chlorine (35·46), bromine (79·92) and mercury (200·6) are shown to consist, in each case, of a mixture of isotopes, the atomic weight of each isotope being an exact whole number.

Thus it seems that Prout's "Whole Number Rule" has, after a century of uncertainty, proved to be substantially true. The only definite exception to the rule that all atomic weights are exact whole numbers is hydrogen, which has an atomic weight 1·008. Theoretical explanations for the slight deviation of this—the lightest of all elements—from the rule have been offered. It seems not unlikely that the atomic weights of certain other elements may differ very slightly from whole numbers; for instance, that the mass of the nitrogen atom may be 14·016.[1]

If once it be admitted that many of the so-called elements are really mixtures of two isotopes, a good many other puzzling facts receive an explanation. Chemists have long been troubled by the fact that the atomic weight of tellurium exceeds that of iodine, although it clearly occupies a place prior to it in the Periodic Table. Much work has been devoted in the past to attempting by chemical means to show that "tellurium" is really a mixture of two substances, the more important component having a true atomic weight below that of iodine. All attempts to resolve it into two substances failed. But if, as is now believed, the two components are really isotopes, the former failure to separate them chemically need occasion no surprise.

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[1] Sir E. Rutherford and J. Chadwick, *Phil. Mag.* **42** (1921), 825.

Further, if it be admitted that the weights of individual atoms are approximately whole numbers, it is legitimate to speculate on the way in which the atomic nucleus is built up.[1] It would seem that the nucleus of all atoms is made up by combination of units having atomic weight approximately 1·0, and this common unit is presumably the hydrogen nucleus; the fact that hydrogen appears to be produced when nitrogen suffers bombardment by α-rays gives considerable support to this view. The hydrogen nucleus can thus be regarded as the unit of positive electricity, just as the electron is regarded as the unit of negative electricity. It is necessary to assume that the nucleus of all atoms (except hydrogen) also contains negative electrons, since the atomic number representing the net nuclear charge is never as high as the atomic weight. If we write η for the hydrogen nucleus, and β for the electron, then the α-particle (or helium nucleus) may be written $\eta_4\beta'_2$; for it has a mass of four units, and a net positive charge of two units.

Probably, the nuclei of the higher (radioactive) atoms contain α-particles as such, since α-particles are given off so frequently in radioactive changes. It is also worthy of attention that several of the commonest elements have atomic weights which are exact multiples of 4, and in these cases the atomic nuclei are possibly made up by the union of α-particles. The elements having atomic weights divisible by four actually make up 85 per cent. of the earth's crust, and 93 per cent. of the material of meteorites, which are the only samples which we receive of the extra-terrestrial universe. If we agree that "abundance" is a measure of "atomic stability," then it would appear that atoms having weights which are exact multiples of that of the α-particle are exceptionally stable. Harkins represents the structures of these atoms thus:—

		Atomic Weight.
Helium	α	4
Carbon	α_3	12
Oxygen	α_4	16
Neon	α_5	20
Magnesium	α_6	24
Silicon	α_7	28
Sulphur	α_8	32

Those elements which have not atomic weights equal to exact multiples of four must be imagined to contain extra hydrogen nuclei in addition to α-particles. This suggestion has received confirmation from recent work by Rutherford and Chadwick.[1] It was stated early in this chapter that nitrogen (atomic weight 14), when bombarded with α-particles, gives rise to certain swiftly moving particles which are believed to be hydrogen nuclei. It has since been found that boron (11), fluorine (19), sodium (23), aluminium (27), and phosphorus (31) give similar particles, which are probably also hydrogen nuclei. It is noteworthy that none of the elements just mentioned have atomic weights which are multiples of four; elements like carbon (12), oxygen (16) and sulphur (32), which have atomic weights equal to exact multiples of four, show no such effect. It is concluded therefore that atoms of the former class contain (in addition to a closely packed nucleus built up of α-particles of mass 4), two or three hydrogen nuclei probably moving round the main nucleus in small orbits as satellites; when such elements are bombarded with α-particles, a hydrogen satellite may occasionally be knocked away from the main nucleus, and escapes from the system as one of the swiftly moving particles referred to above.

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[1] W. D. Harkins, *Phys. Rev.* **15** (1920), 73; *Phil. Mag.* **42** (1921), 305.

List of Radioactive Substances. To complete the chapter, a list is given of the known radioactive substances, showing the character of the rays given out by each, the period of half-change, the group of the Periodic System to which the element belongs, the chemical character and the usual means of preparation.

In the column indicating the radiation produced, the bracketed symbol (β) or (γ) is intended to denote that β- or γ-rays of low penetrating power are given off.

The period of half-change is itself a key to the intensity of the radioactivity possessed by a substance; those elements having a short period are the most active, but, at the same time, the most ephemeral.

The chemical character is expressed very shortly, because in every case the element is described in the later volumes of this book, or is isotopic with some other element, the properties of which are there described.

Finally, in the right-hand column, reference is made to one possible method of obtaining a preparation containing the individual element in question. Further details of the method—and of alternative methods—must be sought elsewhere.[2] The information given is, however, sufficient to make clear what has been stated above, namely that only the stable, long-lived materials occur in the ores in sufficient quantity to make their direct extraction practicable. The short-lived substances must be "grown" in the laboratory.

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[1] Sir E. Rutherford and J. Chadwick, *Phil. Mag.* 42 (1921), 809.

[2] F. Soddy, "Chemistry of Radioactive Elements" (Longmans, Green

Uranium Family. **Commencement and Radium Branch.**

Name of Element.	Rays.	Period of Half-Change.	Group of Periodic Table.	Chemical Character.	Means of Preparation.
Uranium I . . .	α	$5{\cdot}5 \times 10^9$ years	VIA	Homologue of Tungsten	From ores like Carnotite or Pitchblende. Methods described in Vol. II.
Uranium X_1 . .	(β)	24·6 days	IVA	Isotope of Thorium	By growth from Uranium I. An *old* solution of uranium salt containing a trace of iron is treated with ammonium carbonate, which precipitates uranium X_1 along with the iron.[1]
Uranium X_2 . .	β, γ	1·14 min.	VA	Homologue of Tantalum	By growth from Uranium X_1. A solution of UX_1 salt is filtered through moist tantalic acid, which extracts UX_2.
Uranium II . . .		2×10^6 years (?)	VIA	Isotope of Uranium I	Preparations of uranium X_1 gradually lose their β-ray activity. When the β-ray activity has disappeared, the preparation contains Uranium II.
Ionium	α	7×10^4 years	IVA	Isotope of Thorium	From solution of Pitchblende in nitric acid. Lead, radium, etc., are precipitated as sulphates, and then ionium, thorium, etc., are precipitated as fluorides. Being isotopic they are inseparable from one another.
Radium	α	1,645 years	IIA	Homologue of Barium	From Carnotite or Pitchblende. Methods described in Vol. II.
Radium Emanation (Niton)	α	3·85 days	O	Inert Gas. Homologue of Xenon	By growth from radium salt solution. Evolved on boiling or bubbling air through the solution.
Radium A . . .	α	3·0 minutes	VIB	Isotope of	Main constituent of "active deposit" at moment

Radium B . . .	(β) (γ)	26·7 minutes	IVB	Isotope of Lead	From "active deposit" 20 minutes after deposition. Separated from each other by heating at 600°, which volatilizes radium B, and leaves radium C.
Radium C . . .	β	19·5 minutes	VB	Isotope of Bismuth	
Radium C_2 . . .		1·32 minutes	IIIB		Formed in too small amount for isolation.
Radium C′ . . .	α	10^{-6} seconds (approx.)	VIB	Isotope of Polonium	Too short-lived for isolation.
Radium D . . .	(β) (γ)	16·6 years	IVB	Isotope of lead	By growth from radium emanation, contained in quartz flask. After some weeks the deposit on flask is dissolved in nitric acid and the radium D is then deposited by electrolysis on a cathode.
Radium E . . .	β	5·0 days	VB	Isotope of Bismuth	By growth from radium D. An old solution of a salt of radium D on electrolysis at low current density deposits polonium on cathode, and at higher current density radium E (separation usually incomplete). Polonium can also be obtained from carnotite or pitchblende by precipitation of acidified solution with hydrogen sulphide.
Radium F . . . (Polonium)	α	136 days	VIB	Homologue of Tellurium, but resembles Bismuth	
Radium G . . .	None	Infinite (??)	IVB	Isotope of Lead	From carnotite or pitchblende; separation as for lead.
		URANIUM FAMILY.	**Actinium**	**Branch.**	
Uranium Y . . .	β	25 hours	IVA	Isotope of Thorium	When uranium preparations containing iron are precipitated with ammonium carbonate for the separation of uranium X_1, much uranium Y is mixed with the uranium X_1 prepared.[2] Uranium Y cannot be prepared free from Uranium X_1.
Eka-Tantalum . .	α	$1·2 \times 10^4$ years	VA	Isotope of Uranium X_2	From pitchblende by distillation in current of air and carbon tetrachloride vapour (traces only obtained, mixed with other bodies).

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[1] For alternative methods, see G. Kirsch, *Sitzungsber. Akad. Wiss. Wien.* **129** (1920)

[2] See G. N. Antoneff, *Phil. Mag.* **22** (1911), 419; *Le Radium* **10** (1913), 40

URANIUM FAMILY. **Actinium Branch**—*continued.*

Name of Element.	Rays.	Period of Half-Change.	Group of Periodic Table.	Chemical Character.	Means of Preparation.
Actinium . . .	(β)	20 years	IIIA	Homologue of Lanthanum. Resembles Rare Earths	From pitchblende. After removal of polonium with hydrogen sulphide, iron and rare earths are precipitated with ammonia, and redissolved in hydrochloric acid. Rare earths (including actinium) are precipitated with oxalic acid and fractionally crystallized as double magnesium nitrates.
Radio-actinium . .	a	19·5 days	IVA	Isotope of Thorium	By growth from actinium. Thiosulphate is added to an old acidified solution of actinium salt; the sulphur precipitate carries down radio-actinium.
Actinium X. . .	a	11·4 days	IIA	Isotope of Radium	By growth from actinium. By precipitating a solution of actinium preparation with ammonia and filtering. Actinium X remains in filtrate.
Actinium Emanation	a	3·9 seconds	O	Isotope of Radium Emanation	By growth from actinium. Liberated on passing air through an actinium preparation.
Actinium A . . .	a	·002 seconds	VIB	Isotope of Polonium	Too short-lived for isolation.
Actinium B . . .	(β) (γ)	36·1 minutes	IVB	Isotope of Lead	Constituents of "Active Deposit" formed by actinium emanation on walls of vessels. Separated by heat; Actinium B volatilizes more readily than Actinium C.
Actinium C . . .	a	2·15 minutes	VB	Isotope of Bismuth	
Actinium D . . .	β, γ	4·77 minutes	IIIB	Isotope of Thallium	Acid solution of Active Deposit is treated with animal charcoal, which adsorbs Actinium D.
Actinium E . . .	None	Infinite (??)	IVB (?)	Isotope of Lead (?)	

THORIUM FAMILY.

Thorium	α	$1{\cdot}7 \times 10^{10}$ years	IVA	Homologue of Zirconium	From ores such as monazite or thorite. See Vol. II. Extracted on large scale for Mantle Industry.
Mesothorium 1 . . .	(β)	6·7 years	IIA	Isotope of Radium	Bye-product of Mantle Industry. See Vol. II.
Mesothorium 2 . . .	$\beta\,(\gamma)$	6·2 hours	IIIA	Isotope of Actinium	By growth from mesothorium 1; separated from it by precipitation with ammonia.
Radio-thorium . . .	α	696 days	IVA	Isotope of Thorium	By growth from mesothorium. A trace of zirconium is added to the solution and ammonia added. The precipitate of zirconium hydroxide carries down the radio-thorium.
Thorium X	α	3·7 days	IIA	Isotope of Radium	By growth from thorium. Old thorium solution is treated with ammonia which precipitates thorium and radiothorium, and leaves thorium X in filtrate.
Thorium Emanation	α	54 seconds	O	Isotope of Radium Emanation	By blowing air over a thorium preparation which has been stored long enough to develop thorium X.
Thorium A	α	0·14 seconds	VIB		Too short-lived for isolation.
Thorium B	(β)	10·6 hours	IVB		Constituents of Active Deposit. Separated by distilling away the more volatile thorium B.
Thorium C	$\alpha,\ \beta$	60 minutes	VB		
Thorium C′ . .	α	10^{-11} seconds	VIB	Isotope of Polonium	Too short-lived for isolation.
Thorium D . .	$\beta,\ \gamma$	3·1 minutes	IIIB	Isotope of Thallium	Separated from solution of active deposit by addition of potassium salt, followed by platinichloric acid. The precipitate of potassium platinichloride carries down the thorium D.
Thorium E	None	Infinite (??)	IVB	Isotope of Lead(?)	

Summary. Radioactive substances give off continuously either α-particles (identical with helium nuclei) or β-particles (free electrons). The expulsion of β-particles is often accompanied by the production of γ-rays (which are analogous to X-rays). All these rays affect a photographic plate, and cause certain phosphorescent substances to glow. The α-particles when striking matter cause a rise of temperature, sometimes chemical decomposition, and, in the case of gases, ionization; this latter property, which is possessed also by β- and γ-rays, is used for the measurement of radioactivity. In certain cases, bombardment by α-particles may cause the disintegration of the nuclei of other atoms, with the formation of H-particles, or hydrogen nuclei.

The atoms which lose α- or β-particles themselves suffer change in the process; this radioactive change differs from chemical change in that the velocity is independent of temperature, solvents, catalysts, or state of combination. Uranium I in losing an α-particle, generates uranium X_1, which loses a β-particle, yielding uranium X_2. The changes continue until at last we come to radium G, which is chemically identical with lead, and which appears to be stable. The so-called "lead" of uranium minerals is mainly radium G, differing from ordinary lead in having an abnormally low atomic weight. On the other hand, the so-called "lead" of thorium minerals has an abnormally high atomic weight, and is probably mainly thorium E, the end-product of the "thorium series." Most uranium minerals have reached a state of "radioactive equilibrium"; the ratio Ra : U is constant for minerals of different geological ages, but the ratio Pb : U (or strictly RaG : U) increases with the age of the mineral. All these minerals contain "long-lived" elements (such as uranium, radium, thorium and mesothorium I) in quantities sufficient to make their extraction possible; the elements with short periods occur only in minute quantities in minerals and must be prepared by "growth" in the laboratory.

When an element loses an α-particle, it changes to an element occupying a space two places to the left in the Periodic Table; if a β-particle is expelled, there is a shift of one place to the right. By this rule, the chemical character of radioactive substances can be predicted. We frequently find several elements occupying a single space in the periodic table; they are chemically identical—for all practical purposes—but differ in atomic weight and radioactive character; such elements are called "isotopes." Radioactive isotopes cannot be separated by chemical means, but can in most cases be prepared free from one another, by "growth" under suitable conditions.

It is now known that non-radioactive elements, which have atomic weights that are not whole numbers, are really mixtures of isotopes. For instance, two separate methods (one depending on diffusion, and one upon the deflection of positive rays) appear to indicate that chlorine, with "average atomic weight" 35·46, is really a mixture of two atoms of atomic weights 35 and 37.

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A BRIDGED FORM OF PERIODIC TABLE.

O.	IA.	IIA.	IIIA.	IVA.	VA.	VIA.	VIIA.	Transition Elements.			IB.	IIB.	IIIB.	IVB.	VB.	VIB.	VIIB.	O.
2 He	3 Li	4 Be	5 B											6 C	7 N	8 O	9 F	10 Ne
10 Ne	11 Na	12 Mg	13 Al											14 Si	15 P	16 S	17 Cl	18 A
18 A	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 —	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
54 Xe	55 Cs	56 Ba	57 La ↓ 57–71 Rare Earth Metals	58 Ce ↙														
					73 Ta	74 W	75 —	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 —	86 Nt
86 Nt	87 —	88 Ra	89 Ac	90 Th	91 UX_2	92 U												